

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
 United States Patent and Trademark
 Office
 Box PCT
 Washington, D.C. 20231
 ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 14 September 2000 (14.09.00)	
International application No. PCT/GB00/00513	Applicant's or agent's file reference SCB/51358001
International filing date (day/month/year) 15 February 2000 (15.02.00)	Priority date (day/month/year) 16 February 1999 (16.02.99)
Applicant PICKERING, Stephen et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 13 July 2000 (13.07.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Juan Cruz Telephone No.: (41-22) 338.83.38
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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SCB/51358001	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 00/ 00513	International filing date (day/month/year) 15/02/2000	(Earliest) Priority Date (day/month/year) 16/02/1999
Applicant EUROPEAN COMMUNITY, represented by THE COMMISSION;		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

3A _____

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No.

PC./GB 00/00513

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B13/32 C01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 03252 A (RODEL INC) 2 February 1995 (1995-02-02) claim 1	1
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 112 (C-0815), 18 March 1991 (1991-03-18) & JP 03 005324 A (KAWASAKI STEEL CORP), 11 January 1991 (1991-01-11) abstract	1
A	US 5 064 791 A (OHTSUKA KUNIO ET AL) 12 November 1991 (1991-11-12) column 4, line 38 - line 57	1
A	EP 0 712 175 A (STARCK H C GMBH CO KG) 15 May 1996 (1996-05-15) page 2, line 19 - line 36	1

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

25 May 2000

Date of mailing of the international search report

05/06/2000

Name and mailing address of the ISA

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Authorized officer

Clement, J-P

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/00513

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 202 (C-432), 30 June 1987 (1987-06-30) & JP 62 027310 A (TOKUYAMA SODA CO LTD), 5 February 1987 (1987-02-05) abstract -----	1
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 246 (C-439), 11 August 1987 (1987-08-11) & JP 62 052129 A (TOKUYAMA SODA CO LTD), 6 March 1987 (1987-03-06) abstract -----	1



INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00513

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9503252 A	02-02-1995	US 5389352 A EP 0665817 A JP 8501768 T	14-02-1995 09-08-1995 27-02-1996
JP 03005324 A	11-01-1991	NONE	
US 5064791 A	12-11-1991	JP 3050147 A JP 6076244 B DE 4023001 A FR 2649973 A GB 2233970 A,B	04-03-1991 28-09-1994 24-01-1991 25-01-1991 23-01-1991
EP 0712175 A	15-05-1996	DE 4439987 A CA 2162215 A DE 59504730 D ES 2126198 T FI 955349 A JP 8217458 A NO 954487 A US 5599436 A	15-05-1996 10-05-1996 18-02-1999 16-03-1999 10-05-1996 27-08-1996 10-05-1996 04-02-1997
JP 62027310 A	05-02-1987	JP 1633793 C JP 2062481 B	20-01-1992 25-12-1990
JP 62052129 A	06-03-1987	NONE	

INTERNATIONAL COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 04 MAY 2001

WIPO


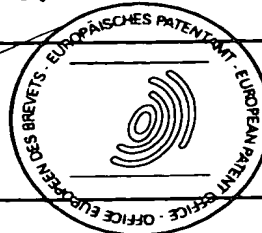
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Applicant's or agent's file reference SCB/51358/001	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB 00/ 00513	International filing date (day/month/year) 15/02/2000	Priority date (day/month/year) 16/02/1999
International Patent Classification (IPC) or national classification and IPC C01B13/32		
Applicant EUROPEAN COMMUNITY,... et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This **REPORT** consists of a total of 4 sheets, including this cover sheet.
☒ This report is also accompanied by **ANNEXES**, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
These annexes consists of a total of 5 sheets.

- This report contains indications relating to the following items:
 - ☒ Basis of the report
 - ☐ Priority
 - ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - ☐ Lack of unity of invention
 - ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - ☐ Certain documents cited
 - ☐ Certain defects in the international application
 - ☐ Certain observations on the international application

Date of submission of the demand 13/07/2000	Date of completion of this report - 2. 05. 01
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+ 49-89) 2399-0, Tx: 523656 epmu d Fax: (+ 49-89) 2399-4465	Authorized officer Bernard Louis Poth 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

I. Basis of the report

1. This report has been drawn up on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*

☐ the international application as originally filed

☒ the description, pages 1-25, as originally filed
 pages, filed with the demand
 pages, filed with the letter of

☒ the claims, Nos., as originally filed
 Nos., as amended under Article 19
 Nos., filed with the demand
 Nos. 1-27, filed with the letter of 20.03.01

☒ the drawings, sheets / fig. 1/7 - 7/7, as originally filed
 sheets / fig., filed with the demand
 sheets / fig., filed with the letter of

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.
☐ the drawings, sheets / fig.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2 (c)).

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/GB00/00513

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Claims	2, 3, 18, 20, 21, 25	YES
	Claims	1, 4-17, 19, 22-24, 26, 27	NO
Inventive Step	Claims		YES
	Claims	2, 3, 18, 20, 21, 25	NO
Industrial Applicability	Claims	1-27	YES
	Claims		NO

2. Citations and Explanations

1. Numerous conventional methods would appear to be based on the concept of adding the oxidant under conditions such that mixing is achieved before substantial precipitation occurs.

Document (1) WO-A-95/03252 confirms if necessary that the process of claim 1 is known. Regarding the prior cooling, it has been noted by this Authority that cooling appears to be used in Example 5 if the exothermal reaction occurs at room temperature, and concentrations in the same order are used in connection with the preferred cations, anions, hydrogen peroxide and ammonium hydroxide.

The remarks of the Applicant in this respect are not convincing. No indication of the reaction temperature is provided in claim 1, nor figures regarding the degree of cooling or the inlet temperature. Tap water for instance would inherently be provided at temperatures below the reaction temperature in Example 5, and said example clearly discloses a formation of the crystallites at room temperature.

2. The additional features of claims 4-17 and 19 all appear to be disclosed in said document.
3. Nanocrystalline powders and their uses as defined in claims 22 to 24, 26 and 27 are also known from document (1).

4. Nothing inventive can be seen in the preferred features of claims 2, 3, 18, 20, 21 and 25. In particular document (1) clearly shows that lower reaction temperatures are preferred to achieve nanocrystalline powders and that hydrothermal treatments can be used if desired. The comparisons made by the Applicant are not significant. Examples 1 to 3 of document (1) are not based on the use of an oxidant, and thus do not provide any teaching on the influence of the reaction temperature in this case. On the contrary the Examples 5 and 6 appear significant, in that a direct relationship can be seen between temperature and properties of the precipitate.

To be noted that the arguments on the influence of the inlet temperature in the claimed process are not convincing. The description does not provide any evidence that any improvement is achieved within the broad scope of claim 1, but only in connection with the embodiment C based on the further addition of ammonium hydroxide.

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Claims:

1. A process for inducing homogeneous precipitation
of a metal oxide, wherein said metal is capable of
5 existing in at least two cationic oxidation states,
which process comprises the steps of:

- (i) providing an aqueous solution of a metal in a
lower cationic oxidation state, and
10
(ii) adding an oxidant capable of oxidizing said metal
to a higher cationic oxidation state under
conditions such that the mixing of said aqueous
solution and said oxidant is substantially
15 complete before precipitation of an oxide of said
metal in its higher oxidation state occurs,

wherein the rate of oxidation is reduced by cooling
the aqueous solution of said metal in a lower cationic
20 oxidation state and/or the oxidant prior to mixing.

2. A process as claimed in claim 1, wherein the
aqueous solution of said metal in a lower cationic
oxidation state and the oxidant are cooled to a
25 temperature in the range of from -10 to 10°C prior to
mixing.

3. A process as claimed in claim 2, wherein the
aqueous solution of said metal in a lower cationic
oxidation state and the oxidant are cooled to a
30 temperature in the range of from 0 to 5°C prior to
mixing.

4. A process as claimed in any one of the preceding
35 claims, wherein the metal oxide which precipitates out
of solution is a product of hydrolysis of the metal in



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its higher cationic oxidation state.

5. A process as claimed in any one of the preceding claims, wherein the oxidant is added as an aqueous solution.

6. A process as claimed in any one of the preceding claims, wherein the metal is selected from Ce or Fe.

7. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state comprises nitrate as a counter-ion.

8. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/l.

9. A process as claimed in any one of the preceding claims, wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/l.

10. A process as claimed in any one of the preceding claims, wherein the oxidant comprises hydrogen peroxide.

11. A process as claimed in claim 10, wherein the metal salt or oxide has the general formula $M(OH)_x \cdot yOOH_y$, wherein X is equal to the oxidation state of the metal cation M and $y \geq 1$.

12. A process as claimed in claim 10 or claim 11, wherein the metal in its lower oxidation state is Ce^{3+} , the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general

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formula $\text{Ce}(\text{OH})_{4-y}\text{OOH}_y$, wherein $y \geq 1$.

13. A process as claimed in any one of the preceding claims, comprising the additional step of adding
5 hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.

14. A process as claimed in claim 13, wherein said
10 hydroxide ions are provided by the addition of ammonium hydroxide.

15. A process as claimed in any one of the preceding claims, comprising the further step of isolating the precipitate.

16. A process as claimed in claim 15, comprising the further step of washing and drying the isolated precipitate.

20 17. A process for the precipitation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of:

25 (i) inducing homogeneous precipitation of said metal oxide by a process according to claim 13 or claim 14; and

(ii) isolating the precipitate.

30 18. A process as claimed in claim 17, which further comprises the step of subjecting the precipitate to hydrothermal treatment.

35 19. A process as claimed in claim 17 or claim 18 comprising the further step of washing and drying the precipitate.

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20. A process as claimed in any one of claims 17 to 19, wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

5 21. A process as claimed in any one of claims 17 to 20, wherein said hydrothermal treatment is at a temperature of approximately 180°C.

10 22. A metal oxide obtained by a process as claimed in any one of claims 1 to 16.

15 23. A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in any one of claims 17 to 21.

20 24. A metal oxide as claimed in claim 22 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 having a mean particle size in the range of from 2 to 10 nm with a geometric standard deviation in the particle size less than or equal to 1.2.

25 25. A metal oxide as claimed in claim 22 or claim 24 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 23 or claim 24 having a mean particle size in the range of from 2 to 5 nm with a geometric standard deviation in the particle size less than or equal to 1.1.

30 26. A metal oxide as claimed in any one of claims 22, 24 or 26 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in any one of claims 23, 24 or 25 which comprises cerium oxide.

35 27. A glass, a polishing medium for glass, a thin surface film, a phosphor, an oxygen storage material or catalyst material which has been manufactured by a

AMENDED SHEET

Empfangszeit 20.März 20:13

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process which uses a weakly agglomerated
nanocrystalline powder of a metal oxide as claimed in
any one of claims 23, 24, 25 or 26.

Claims

1. A process for inducing homogeneous precipitation
of a metal oxide, wherein said metal is capable
of existing in at least two cationic oxidation
states, which process comprises the steps of,
(i) providing an aqueous solution of a metal in
a lower cationic oxidation state and,
(ii) adding an oxidant capable of oxidising said
metal to a higher cationic oxidation state
under conditions such that the mixing of
said aqueous solution and said oxidant is
substantially complete before precipitation
of an oxide of said metal in its higher
oxidation state occurs.
2. A process as claimed in claim 1 wherein the
metal oxide which precipitates out of
solution is a product of hydrolysis of the
metal in its higher cationic oxidation
state.
3. A process as claimed in claim 1 or claim 2
wherein the oxidant is added as an aqueous
solution.
4. A process as claimed in any one of the
preceding claims wherein the metal is
selected from Ce or Fe.
5. A process as claimed in any one of the
preceding claims wherein the aqueous
solution of said metal in a lower cationic
oxidation state comprises nitrate as a
counter-ion.

- 5 6. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/l.
- 10 7. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/l
- 15 8. A process as claimed in any one of the preceding claims wherein the oxidant comprises hydrogen peroxide.
- 20 9. A process as claimed in claim 8 wherein the metal salt or oxide has the general formula $M(OH)_{x-y}OOH_y$ wherein x is equal to the oxidation state of the metal cation M and $y \geq 1$.
- 25 10. A process as claimed in claim 8 or claim 9 wherein the metal in its lower oxidation state is Ce^{3+} , the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.
- 30 11. A process as claimed in any one of the preceding claims wherein the rate of oxidation is reduced by cooling the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant prior to
- 35 mixing.

- 5 12. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant are cooled to a temperature in the range of from -10 to 10°C prior to mixing.
- 10 13. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant are cooled to a temperature in the range of from 0 to 5°C prior to mixing.
- 15 14. A process as claimed in any one of the preceding claims comprising the additional step of adding hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.
- 20 15. A process as claimed in claim 14 wherein said hydroxide ions are provided by the addition of ammonium hydroxide.
- 25 16. A process as claimed in any one of the preceding claims comprising the further step of isolating the precipitate.
- 30 17. A process as claimed in claim 16 comprising the further step of washing and drying the isolated precipitate.
- 35 18. A process for the preparation of a weakly agglomerated nanocrystalline powder of a metal oxide which process comprises the

steps of,

- i) inducing homogeneous precipitation of said metal oxide by a process according to claim 14 or claim 15.
- ii) isolating the precipitate.

19. A process as claimed in claim 18 which further comprises the step of subjecting the precipitate to hydrothermal treatment.

20. A process as claimed in claim 18 or claim 19 comprising the further step of washing and drying the precipitate.

21. A process as claimed in any one of claims 18 to 20 wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

22. A process as claimed in any one of claims 18 to 21 claim wherein said hydrothermal treatment is at a temperature of approximately 180°C.

23. A metal oxide obtained by a process as claimed in any one of claims 1 to 17.

24. A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in any one of claims 18 to 22.

25. A metal oxide as claimed in claim 23 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 24 having a mean particle size in the range of

from 2 to 10nm and with a geometric standard deviation in the particle size less than or equal to 1.2.

- 5 26. A metal oxide as claimed in claim 23 or
 claim 25 or a weakly agglomerated
 nanocrystalline powder of a metal oxide as
 claimed in claim 24 or claim 25 having a
10 mean particle size in the range of from 2 to
 5 nm with a geometric standard deviation in
 the particle size less than or equal to 1.1.
27. A metal oxide as claimed in any one of
 claims 23, 25 or 26 or a weakly agglomerated
15 nanocrystalline powder of a metal oxide as
 claimed in any one of claims 24, 25 or 26
 which comprises cerium oxide.
28. A glass, a polishing medium for glass, a
20 thin surface film, a phosphor, an oxygen
 storage material or a catalyst material
 which has been manufactured by a process
 which uses a weakly agglomerated
25 nanocrystalline powder of a metal oxide as
 claimed in any one of claims 24, 25, 26 or
 27.

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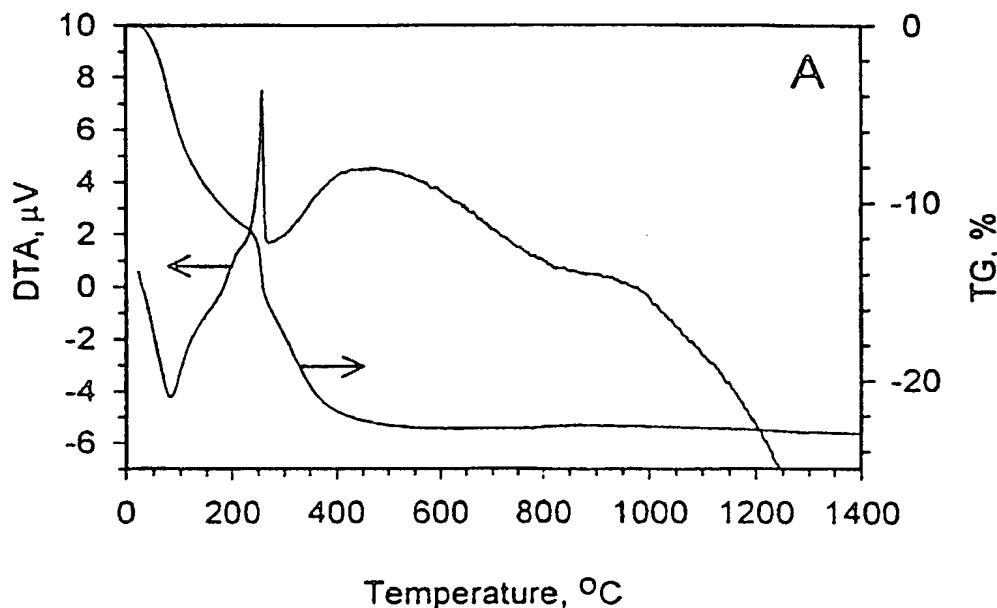
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C01B 13/32, C01F 17/00	A1	(11) International Publication Number: WO 00/48939 (43) International Publication Date: 24 August 2000 (24.08.00)
(21) International Application Number: PCT/GB00/00513 (22) International Filing Date: 15 February 2000 (15.02.00) (30) Priority Data: 9903519.8 16 February 1999 (16.02.99) GB (71) Applicant (for all designated States except US): EUROPEAN COMMUNITY, represented by THE COMMISSION OF THE EUROPEAN COMMUNITIES [LU/LU]; rue Alcide de Gasperi, L-2920 Luxembourg (LU). (72) Inventors; and (75) Inventors/Applicants (for US only): PICKERING, Stephen [GB/NL]; Noordlaan 14, NL-1861 GN Bergen (NL). DJURICIC, Boro [NL/NL]; Mozartlaan 10, NL-1817 GS Alkmaar (NL). (74) Agent: BOULT WADE TENNANT; Verulam Gardens, 70 Gray's Inn Road, London WC1X 8BT (GB).		(81) Designated States: CA, JP, NO, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: PRECIPITATION PROCESS



(57) Abstract

The present invention relates to a process for inducing homogeneous precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of: i) providing an aqueous solution of a metal in a lower cationic oxidation state; and ii) adding an oxidant capable of oxidising said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation of an oxide of said metal in its higher oxidation state occurs.



FOR THE PURPOSES OF INFORMATION ONLY

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Precipitation Process

The present invention is concerned with a process for inducing homogeneous precipitation of metal oxides and with the application of such a process to the preparation of weakly agglomerated nanocrystalline powders of said metal oxides.

In the present specification the term "metal oxides" is intended to include hydroxides, hydrated oxides, oxohydroxides, or oxoperoxohydroxides of metals.

The increased mechanical performance demanded of advanced ceramic materials imposes increasingly stricter requirements on the ceramic powders from which they are made. The use of monodisperse nanocrystalline powders as starting materials has demonstrated considerable potential for improving the functional properties of existing ceramic compositions. For example, the use of monodisperse nanocrystalline powders as starting materials provides ceramic compositions with finer porosity (e.g. for use in ceramic filters), and greater surface area (e.g. for use in catalysts). Such materials are also capable of forming better thin ceramic coatings.

In the present specification the term "nanocrystalline powder" is intended to mean a powder wherein substantially all of the constituent particles have a crystal size of less than 100nm.

The term "weakly agglomerated powder" is intended to mean a powder containing agglomerates that break up during normal processing or forming operations.



The term "monodisperse powder" is intended to mean a powder whose particle size distribution has a geometric standard deviation, σ_g , less than or equal to 1.1. For many conventional powders σ_g would be in the range of from 1.8 to 2.2.

Cerium (IV) oxide, CeO_2 , is an example of a material where the number of applications has increased rapidly, for example in glasses, phosphors, catalysis, and chemical applications, and for which the use of nanocrystalline powders is an important factor. Unfortunately, the high specific surface areas of nanocrystalline powders, in which the primary particle size is often smaller than 5nm, also results in a stronger tendency of the powder to agglomerate which can make processing difficult. In the present specification the term "primary particle" distinguishes the small individual particles (typically less than 5nm in diameter) that are formed in the first stage of the homogeneous precipitation process from the larger agglomerates of such particles (typically 50-100nm in diameter) that may form later. These large spherical agglomerates are referred to as "secondary particles" and may contain hundreds of primary particles. Weakly-agglomerated powder is needed both for dry processing methods, for example powder compaction, and for the preparation of stable suspensions in liquids, for example for thin or thick film production. Unless weakly-agglomerated nanoscale powders can be produced, the benefits expected from highly-uniform nanocrystalline powders are easily lost during the manufacture of components. The strength of agglomerates depends on the surface properties of the nanocrystalline particles in the powder and these properties are sensitively dependent on the powder



synthesis procedures.

Precipitation from aqueous metal salt solution is widely used in industry for producing ceramic oxide powders, but for nanocrystalline materials, such powders tend to form excessively hard agglomerates. The precipitated species is usually a precursor, for example a hydroxide, rather than the required oxide and a thermal decomposition treatment is needed to obtain the final product. In densely agglomerated nanostructured powders there are many points of contact between primary particles and even a low-temperature thermal decomposition treatment allows sufficient diffusion to occur to produce agglomerates too hard to be easily redispersed. Dense agglomerates must therefore be avoided during the precipitation process if easily processable powders are to be obtained. Control of agglomerate morphology requires control of the chemistry of the precipitation reaction.

Precipitation occurs by adding a precipitating ligand (anion) to a solution containing cations of the appropriate metal. If the precipitating ligand is added directly by simply pouring one solution into another then there is little control of the chemistry during precipitation because of the large and inhomogeneous gradients in solution concentration. A better control of chemical and morphological characteristics can be achieved if the precipitating ligands are generated "in situ", simultaneously and uniformly throughout the solution, this results in what is known as a "homogeneous" precipitation process.

A homogeneous precipitation process based on forced hydrolysis is quite widely applicable and has been used to produce various monodisperse metal oxide precursor particles of various shapes and sizes [see
5 MATIJEVIC, in High Tech Ceramics, edited by P.Vincenzini, (Elsevier, Amsterdam, 1987) p. 441-458]. Forced hydrolysis is usually accomplished either by increasing the pH of the solution, or by heating the solution, in some cases at temperatures up to boiling
10 point at atmospheric pressure, but more usually to higher temperatures under pressure, i.e. hydrothermal treatment.

In the present specification, the term "hydrothermal
15 treatment" of a substrate means heating said substrate in the presence of water at a temperature above the normal boiling point of the water under applied or autogenous pressure sufficient to prevent boiling of the water.

20 Homogeneous precipitation by an increase in the pH of the solution can be achieved by the thermal decomposition of urea or hexamethylenetetramine to form ammonia thereby generating OH^- as the
25 precipitating ligand [see MATIJEVIC, in High Tech Ceramics, edited by P.Vincenzini, (Elsevier, Amsterdam, 1987) p. 441-458]. Monodispersity of the precipitated particle results from the occurrence of nucleation in a single burst followed by a uniform
30 growth process, for example according to the LaMer theory. The primary particles resulting from such a nucleation process are usually monodisperse and several nanometers in size. Amorphous precipitates such as aluminium hydroxide usually consist of
35 spherical particles whereas crystalline precipitates



often consist of faceted particles. Ageing of such a solution usually leads to agglomeration of the primary particles to form densely packed agglomerates. The agglomerates often have a fairly narrow size distribution and tend to be spherical in the case of amorphous precipitates where there is no ordering force such as a dipole moment or a difference in the surface energy between the crystal facets of the primary particles. Agglomerates as large as 1 micron in diameter can be obtained.

There are several reports of methods for the preparation of cerium oxide that depend on an increase in pH to cause precipitation. Matjevic and Hsu [see MATIJEVIC and W.P.HSU, *J. Colloidal Interface Sci.*, 118 (1987) 506-523] obtained non-spherical crystalline particles of $\text{CeO}(\text{CO}_3)_2\text{H}_2\text{O}$ by precipitation with urea. Aiken et al [see AIKEN, W.P. HSU and E.MATIJEVIC, *J. Am. Ceram. Soc.*, 71 (1988) 845-85] used the same method to obtain spherical particles of a mixed Y(III)/Ce(III) compound. Akinc and Sordélet [see AKINC and D.SORDELET, *Advanced Ceramic Materials*, 2 (1987) 232-238] prepared non-spherical well-crystallised CeOHCO_3 particles. Chen and Chen [see CHEN and I.W. CHEN, *J. Am. Ceram. Soc.*, 76 (1993) 1577-1583] used hexamethylenetetramine decomposition to prepare cerium oxide powders and compared them with those precipitated with ammonium hydroxide.

Heating the solution to force hydrolysis has been reported by several authors. Briois et al [see BRIOIS, C.E.WILLIAMS, H. DEXPERT, F.VILLAIN, B. CABANE, F. DENEUE and C.MAGNIER, *J. Mat. Sci.*, 28 (1993) 5019-5031] reported the preparation of 3nm particles of $\text{CeOSO}_4\text{H}_2\text{O}$ from Ce(IV) sulphate at 90°C, but this is not



an attractive precursor for cerium oxide due to the presence of the sulphate group.

5 Hydrothermal conditions appear more suitable for the direct preparation of cerium oxide. Hirano and Kato [see HIRANO and E. KATO, *J. Am. Ceram. Soc.* 79 (1996) 777-780] obtained fine cerium oxide from Ce(III) nitrate, Ce(IV) sulphate and Ce(IV) ammonium sulphate solutions at 180°C under autogenous pressure. Stable
10 suspensions of well crystallised cerium and cerium oxide doped with 6 at% Y were hydrothermally synthesised at temperatures up to 300°C by Yang and Rahman [see YANG and M.N. RAHAMAN, *J. Eur. Ceram. Soc.*, 17 (1997) 525-535].

15 The homogenous precipitation results cited above, which all depend on forced hydrolysis to cause precipitation succeed in controlling agglomerate morphology and yield agglomerates with a narrow size
20 distribution. However, in the case of precipitation by increase of pH, the agglomerates are densely packed and because the primary particles tend to be strongly bound together by surface forces, the resulting agglomerates are not easily redispersed. Hydrothermal
25 treatment is generally more successful in producing weakly-agglomerated and well-crystallised powders, but the crystallite size tends to be considerably larger. These results demonstrate that powder characteristics are sensitively dependent on the method of preparation
30 so that, in principle, there is considerable scope to try to engineer the powder properties to suit a particular application. Uniformly-sized crystallites smaller than 5nm, or loosely-bound agglomerates have been produced with the methods mentioned above, but
35 obtaining both characteristics in one powder with them



has been difficult to achieve. Forced hydrolysis by increase of pH or temperature is the common factor in these methods, and if it is this that restricts the range of powder properties that can be achieved, then
5 alternative precipitation chemistries are required to provide better routes to weakly-agglomerated nanoscale powders.

It is an object of the present invention to address at
10 least some of the problems associated with methods of homogeneous precipitation known in the art.

Accordingly, in a first embodiment, the present invention provides a process for inducing homogeneous
15 precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of,

- (i) providing an aqueous solution of a metal in a lower cationic oxidation state and,
20 (ii) adding an oxidant capable of oxidising said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation
25 of an oxide of said metal in its higher oxidation state occurs.

The precipitation process of the present invention may include the further step of isolating the resultant
30 precipitate by, for example, filtration, sedimentation, electrophoresis or centrifugation. The process may also further include the steps of washing and drying the isolated precipitate.

35 It is necessary for mixing to be substantially

complete before oxidation sufficient to result in precipitation of said metal oxide has occurred because this means that precipitation is delayed until a homogeneous mixture is formed. This ensures that
5 homogeneous precipitation results.

Preferably, the metal oxide which precipitates out of solution is a product of hydrolysis of the metal in its higher cationic oxidation state. Metal ions in
10 their higher cationic states have a greater charge density than those in their lower cationic oxidation state are therefore frequently more susceptible to hydrolysis in aqueous solution.

15 Metal hydroxides, hydrated metal oxides, metal oxohydroxides, and metal oxoperoxohydroxides (herein referred to collectively as "metal oxides") are commonly the products of metal cation hydrolysis.

20 It will be appreciated by a person skilled in the art that the metal may be selected from many metals which are capable of existing in at least two cationic oxidation states. Preferably, the metal is selected from Ce or Fe. Ce can exist in the +III and +IV
25 oxidation states whilst Fe can exist in the +II and +III oxidation states.

The counter-ion to the metal in its lower oxidation state may be any inorganic anion which provides a
30 soluble salt of the metal in its lower oxidation state. Preferably, the counter-ion is selected from one or more of nitrate, chloride, sulphate, phosphate, fluoride, bromide, and iodide. Most preferably the counter-ion is a nitrate ion because nitrate ions
35 invariably confer high aqueous solubility on their



metal salts.

It will be appreciated by those skilled in the art that the concentration of the aqueous solution of said metal in a lower cationic oxidation state will depend on the identity of the metal ion and its counter-ion and possibly also on the identity of the oxidant used in the process. However, in a preferred embodiment the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/l, preferably 0.05 to 0.2. More preferably, the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/l.

It will also be appreciated by those skilled in the art that a number of suitable oxidants may be used to effect oxidation of the metal from its lower cationic oxidation state to its higher cationic oxidation state. Preferably, the oxidant is present as a solution in a water-miscible solvent, more preferably as an aqueous solution. In a particularly preferred embodiment, the oxidant comprises hydrogen peroxide. Hydrogen peroxide is particularly preferred because it does not contaminate the end product with additional anion species. More preferably, the oxidant comprises an aqueous solution of from 3% to 50% hydrogen peroxide in water. In a still more preferred embodiment the aqueous solution of an oxidant comprises approximately 30% hydrogen peroxide in water. Potassium permanganate is another possible oxidant. Preferably, potassium permanganate is added as an aqueous solution.

When hydrogen peroxide is used as the oxidant the

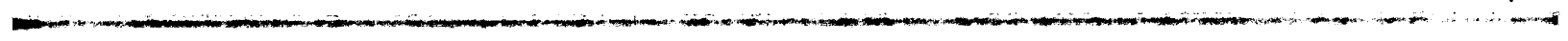


metal oxide which precipitates out of solution may have the general formula $M(OH)_{x-y}OOH_y$ wherein x is equal to the oxidation state of the metal cation M and $y \geq 1$. For example, when the metal in its lower oxidation state is Ce^{3+} and the metal in its higher oxidation state is Ce^{4+} the metal oxide which precipitates out of solution has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.

It will be appreciated by those skilled in the art that a number of suitable methods may be used to reduce the rate oxidation of the metal from its lower cationic oxidation state to its higher cationic oxidation state. However, in a preferred embodiment the rate of oxidation is slowed by cooling the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant (hereinafter referred to as the reactants) prior to mixing. More preferably, both reactants are cooled to a temperature in the range of from $-10^{\circ}C$ to $10^{\circ}C$ prior to mixing. Even more preferably, both reactants are cooled to a temperature in the range of 0 to $5^{\circ}C$ prior to mixing.

The process of the present invention is distinguished from the prior art in that precipitation is induced by a change in oxidation state of the cation and not by an increase in pH or temperature.

Advantageously, the homogeneous precipitation process comprises the additional step of adding hydroxide ions to the mixture of the reactants so as to substantially complete the precipitation process. Preferably, said hydroxide ions are provided by the addition of aqueous ammonium hydroxide. Preferably the ammonium hydroxide has a concentration in the range of from 5 to 33 vol%,



more preferably approximately 25 vol%.

The homogeneous precipitation process of the present invention, including the step of adding hydroxide ions, provides metal oxides which are suitable precursors for the generation of weakly agglomerated nanocrystalline powders of said metal oxides. Accordingly, in a second embodiment, the present invention provides a process for the preparation of a weakly agglomerated nanocrystalline powder of a metal oxide, which process comprises the steps of,

- i) inducing homogeneous precipitation of said metal oxide by a process as hereinbefore described in the first embodiment including the additional step of adding hydroxide ions to the mixture of the first and second solutions so as to substantially complete the precipitation process,
- ii) isolating the precipitate.

Preferably, the process includes the further step of subjecting the isolated precipitate to hydrothermal treatment.

The process may also include the further steps of washing and drying the resultant precipitate.

Step ii) may be achieved, for example, by filtration, sedimentation, electrophoresis or by use of a centrifuge.

Preferably, said hydrothermal treatment comprises heating the precipitate in an autoclave in the presence of water at a temperature of from 100 to



300°C, more preferably, at a temperature of from 150 to 200°C, most preferably, at a temperature of approximately 180°C.

- 5 As stated above the pressure used for the hydrothermal treatment is that sufficient to prevent boiling of the water. This will obviously depend upon the temperature. At lower temperatures, i.e. up to 220°C, sufficient pressure may be generated by the vapour
- 10 pressure of the water in the sealed vessel, i.e. from 5 to 50 bar. At higher temperatures, i.e. greater than 220°C, pressure may need to be applied, i.e. up to 150 bar.
- 15 The present invention also includes within its scope a metal oxide produced by the homogeneous precipitation process as hereinbefore described in the first embodiment.
- 20 The present invention also includes within its scope a weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as hereinbefore described in the second embodiment.
- 25 Preferably, the metal oxide or weakly agglomerated nanocrystalline powder of a metal oxide has a mean particle size in the range of from 2 to 10 nm with a geometric standard deviation, σ_g , less than or equal to 1.2. More preferably in the range of from 2 to 5 nm
- 30 with a geometric standard deviation, σ_g , less than or equal to 1.1.

Particularly preferred metal oxides, and particularly preferred weakly agglomerated nanocrystalline powders

35 of a metal oxide, are those which comprise cerium (IV)



oxide.

The present invention also includes within its scope a glass, a polishing medium for glass, a thin surface
5 film, a phosphor, an oxygen storage material or a catalyst material which has been manufactured by a process which uses a weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as hereinbefore described in
10 the second embodiment.

In a particularly preferred embodiment of the present invention, a nanocrystalline powder of cerium oxide is prepared from aqueous cerium (III) nitrate solution by
15 a two-stage precipitation process which yields weakly-agglomerated powders with a crystallite size smaller than 5nm. In this embodiment a 30% aqueous solution of hydrogen peroxide is added to an aqueous solution of cerium nitrate at 5°C to slowly oxidise Ce^{3+} to Ce^{4+}
20 and thereby initiate homogeneous precipitation of 3-4nm primary particles and the formation of dense spherical agglomerates. The precipitation process is completed by the addition of ammonium hydroxide which disrupts the spherical agglomerates leaving a weakly-
25 agglomerated powder of hydrated cerium oxide. The process is completed by hydrothermal treatment at 180°C.

Precipitation is therefore induced by a change in
30 oxidation state of the cation and not by an increase in pH or temperature. The product of the reaction is believed to be $\text{Ce}(\text{OH})_3\text{OOH}$ and not $\text{Ce}(\text{OH})_4$ which is otherwise obtained when ammonium hydroxide alone is used as the precipitating agent.

35



The present invention will be further illustrated with reference to the following examples and comparative examples

5 The starting materials used in the following examples were: cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, anal., Alfa-Johnson Matthey), hydrogen peroxide (30% H_2O_2 , p.a., Merck) and ammonium hydroxide (NH_4OH , 25 vol% p.a., Merck).

10

Three synthesis routes, referred to as methods A, B and C, were used for preparation of cerium oxide powder as described below.

15

Method A (Comparative Examples A1 and A2)

Ammonium hydroxide was added dropwise to a stirred solution of 0.1 mol/l Ce(III) nitrate in water until a solution pH of 10 was reached. A white or yellowish gel-like precipitate was formed which settled rapidly.

20 A sample of the gel-like initial precipitate was prepared for analysis by taking a portion of the reaction mixture, decanting the solution and washing the precipitate twice with a double volume of distilled water and then drying at 80-85°C overnight

25 (Example A1). The remainder of the product, i.e. supernatant + precipitate, was hydrothermally treated at 180°C for 4 hours under autogenous pressure without stirring to obtain cerium oxide. After cooling, the clear solution was decanted and the yellowish

30 precipitate was washed with about 200ml distilled water and then dried at 80-85°C overnight (Example A2).

Method B (Examples B2 and B3 are Comparative)

35 A solution of 0.1 mol/l Ce(III) nitrate in water was



mixed with 30 vol% hydrogen peroxide in a volume ratio of 3 parts Ce(III) nitrate to 1 part hydrogen peroxide at various temperatures: at about 5°C (Example B1), at room temperature (Example B2), and a solution which
5 was mixed at RT and then heated to boiling temperature (Example B3). An orange-yellow transparent sol appeared in all cases: after 8-10 minutes at 5°C and after 2-3 minutes at RT, or on heating to boiling point. The sol produced at 5°C and aged at that
10 temperature for 12h was stable at room temperature for more than one week without any settling of the solid phase. In contrast, solids produced at room temperature and by heating to boiling partially sedimented. The precipitated solid particles (Examples
15 B1, B2 and B3) were separated by centrifugation for further examination.

Method C

Separate solutions of 0.1 mol/l Ce(III) nitrate in
20 water and of 30 vol% hydrogen peroxide were cooled to 5°C and then mixed together under constant stirring. After 8-10 minutes the solution turned first yellow then orange-yellow, but remained transparent, and a sol was formed. Ammonium hydroxide solution was then
25 added to increase the pH value to 10. Above a pH of 9-9.2 the pH increased only slowly in response to further addition of ammonium hydroxide solution and an orange precipitate settled rapidly from solution. Precipitation therefore occurred in two stages. The
30 solution was decanted and the precipitate was washed and dried at 80-85°C (example C1) or hydrothermally treated (example C2) as described under method A (example A2) above.

35 Samples of the powders synthesised by methods A, B and

C were calcined in air to 300°C and 500°C in alumina crucibles at a heating rate 2°C/min with a dwell time of 1h at temperature.

- 5 The precipitated cerium oxide precursors and calcined products were characterised using several techniques known to those skilled in the art to determine particle size, composition and morphology.
- 10 Differential thermal analysis and thermogravimetric analysis (DTA/TG, Netsch STA 409) were conducted in a dry-air atmosphere using a heating rate of 2°C/min.
- 15 Samples for transmission electron microscopy (TEM, Philips EM 400) of the precipitated cerium oxide precursors were prepared by dipping carbon-coated copper grids into a dilute water suspension of the particles immediately after synthesis. The grids were then dried at room temperature or at 80-85°C. The
- 20 calcined product was dispersed in absolute ethyl alcohol by ultrasonification (3-5 min) and a drop of a suspension was allowed to evaporate on the grid at room temperature. X-ray diffraction analysis (XRD, Philips PW173) was used to determine phase composition and to estimate the crystallite size of the powders. A
- 25 2θ range of 5-80° was used and the apparent crystallite size was estimated from peak broadening using the Scherrer equation: $D_{app} = K \lambda / (B \cos\theta)$, where $K = 0.9$ and $B =$ peak width obtained using a
- 30 Voigt peak fitting routine. CuK_α radiation with a graphite filter was used ($\lambda = 1.5406$) and the instrumental broadening was determined using a LaB_6 standard.
- 35 The precipitates produced by the 3 different methods



differed significantly, primarily due to the presence of different anion species (-OH in method A, -OOH in method B, or -OH + -OOH in method C) and to the reaction temperature used.

5

The use of ammonium hydroxide alone (method A) resulted in voluminous white or yellowish gel-like precipitate from Ce(III) nitrate solution. In principle the precipitate should be $\text{Ce}(\text{OH})_3$, which is white and is a definite compound rather than a hydrous oxide. Oxidation of Ce^{3+} to Ce^{4+} in solution has been suggested at high pH, i.e. $\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ce}(\text{OH})^{3+} + \text{H}^+ + \text{e}^-$ with subsequent hydrolysis to $\text{Ce}(\text{OH})_4$ and precipitation. However, oxidation of $\text{Ce}(\text{OH})_3$ also occurs readily in air at room temperature to form yellow $\text{Ce}(\text{OH})_4$. $\text{Ce}(\text{OH})_4$ is a hydrous oxide which can also be described as $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ which dehydrates progressively i.e. $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ where $n \leq 2$. The product of precipitation with ammonium hydroxide is therefore likely to be $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ rather than $\text{Ce}(\text{OH})_3$.

Precipitation from Ce(III) nitrate using hydrogen peroxide alone (method B) resulted in a fine solid which formed faster at boiling temperature (example B3) than at 5°C (example B1) or at room temperature (example B2). The stability of the solid solution, as defined by the first appearance of settled solid, was more than 1 week for solid produced at 5°C, and a few minutes for solid produced at boiling temperature. Hydrogen peroxide alone was not capable of precipitating all cerium ions from solution. Complete precipitation of cerium ions was achieved using hydrogen peroxide + ammonium hydroxide (method C). The orange-yellow precipitate was formed by a two step process, first the initiation of hydrolysis and



complexation with hydrogen peroxide followed by quantitative precipitation with ammonium hydroxide to a pH of about 10. The precipitate settled rapidly and it was easily separated from solution. The precipitates were stable in water but the dry precipitate slowly transformed to crystalline cerium oxide in air at room temperature.

Cerium oxide was identified in the X-ray diffraction spectra of all the powders. The peaks in the spectra of powders precipitated by ammonia alone (method A) were narrow and well-defined with a high signal-to-noise ratio; those of the other powders were all much broader and less intense. Peak broadening may be attributed to small crystallite size and apparent crystallite sizes were calculated as shown in table 1. The cerium oxide powder derived from the -OH (method A) and -OOH + -OH (method C) precipitates by hydrothermal treatment (examples A2 and C2) were both weakly agglomerated, but the powder from mixed ligand precipitation had a significantly smaller apparent crystallite size (4.2nm compared with 26.8nm).

Information about the chemical composition of the precipitates was deduced from the thermogravimetric weight loss measurements by comparing measured values with the theoretical weight losses for plausible decomposition reactions e.g. the decomposition of hydrated oxide i.e., $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ to CeO_2 should result in a weight loss of 17.29%. The XRD spectra indicated that CeO_2 was present in all samples, but the additional presence of amorphous $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot n\text{H}_2\text{O}$ could not be excluded.

The precipitate obtained by method A (addition of



ammonium hydroxide alone) after drying overnight at 80-85°C (example A1) showed a weight loss of 6.2% and a weight loss of 3.1% after hydrothermal treatment (example A2), as shown in Figures 1A and 1B. These weight losses are lower than those corresponding to the decomposition of $\text{Ce}(\text{OH})_3$ (9.95%) or $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ (17.3%) and indicate that the samples consisted either of a partially hydrated form of cerium oxide, i.e. $\text{CeO}_2 \cdot n\text{H}_2\text{O}$, for which a 6.2% weight loss on decomposition corresponds to $n = 0.59$, or that it consisted of a mixture of phases e.g. $\text{CeO}_2 + \text{CeO}_2 \cdot 2\text{H}_2\text{O}$. A weak exothermic peak at about 280°C, which might correspond to the crystallisation of anhydrous cerium oxide, was clearly present in Figure 1A, but was scarcely evident in Figure 1B for the hydrothermally treated sample.

The precipitate obtained by method B (precipitation with hydrogen peroxide alone) showed a total weight loss of 16.8% for the precipitation procedure carried out at boiling point as shown in figure 2. This total weight loss corresponds well with that expected for $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ decomposition (17.3%). The general shape of the weight loss curve was similar to that in Figures 1A and 1B, i.e. the decomposition appeared to occur in 3 distinct stages and was not complete until >800°C, but the DTA curve did not show the exothermic peak at 280°C that was observed in Fig 1A.

The precipitate obtained by method C (precipitation with hydrogen peroxide followed by ammonium hydroxide) at 5°C showed a total weight loss of 23.0% as shown in Fig 3 which corresponds closely to that expected for the decomposition of $\text{Ce}(\text{OH})_3\text{OOH}$ (23.2%) assuming that a single phase was initially present. The DTA curve in



Fig 3A showed two well-defined events. The first event produced an endothermic peak at about 80°C, which might be due to dehydration, or it might correspond to the transformation; $\text{Ce}(\text{OH})_3\text{OOH} \rightarrow \text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$, with a theoretical weight loss of 7.1%. The second event generated a well-defined exothermic peak at 250-280°C which might correspond to the crystallisation of CeO_2 occurring at a slightly lower temperature than in the case of that obtained with method A (see Fig 1A). After ageing freshly-prepared precipitate for 4h at 100°C the TG weight loss was 15.1% which does not correspond to the decomposition of any single compound and would be consistent with the presence of a mixture of species due to the complete decomposition of the initial phase e.g. of $\text{Ce}(\text{OH})_3\text{OOH}$ to $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ and the partial decomposition of $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ to $\text{CeO}_2 \cdot n\text{H}_2\text{O}$ where $n < 2$. The DTA curve was consistent with the interpretation of the TG curve given above i.e. it no longer showed an endothermic peak at 80°C and the exothermic peak at 250-280° was still present but was slightly less intense compared with that for the precipitate prepared at 5°C.

TEM analysis provided information on the size and shape of primary particles and their state of agglomeration. The general morphology of the particles precipitated by ammonium hydroxide (method A) is shown in Fig 4A. The precipitate consisted of non-uniform agglomerates of equiaxed crystallites approximately 3-4nm diameter. On calcination there was considerable grain coarsening and the agglomerates were hard and non-dispersable Fig 4B. Hydrothermal treatment of the hydroxide precipitate resulted in non-agglomerated uniform cubic crystallites 15-20 nm in diameter as shown in Fig 4C. The hydrothermally treated powder



exhibited considerable coarsening of crystallite size after calcination for 1h at 300°C, Fig 4D.

5 Particles obtained by precipitation with hydrogen peroxide (method B) at room temperature (example B2) consisted of dense agglomerate of crystallites 3-4nm in diameter as shown in Figures 5A and 5B.

Crystallisation of cerium oxide could be observed under the electron beam during TEM examination.

10 Figures 5C and 5D shows particles produced by precipitation with hydrogen peroxide at 5°C (example B1). The crystallites were slightly smaller at 2-3nm than in the sample precipitated at room temperature.

15 Figures 5E and 5F show particles precipitated by hydrogen peroxide at 85°C (example B3). The densely-packed equiaxed agglomerates of 50-100 nm diameter that were obtained are typical of agglomerates formed during homogeneous precipitation and consisted of randomly oriented primary crystallites of 3-4nm i.e. similar in size to those precipitated at RT.

20 Crystallite size coarsened considerable on calcination. Sharply-faceted crystallites as large as the agglomerates were observed after 1h at 300°C - Fig 5G.

25 Particles from the two-stage precipitation at 5°C with hydrogen peroxide and ammonium hydroxide (method C) are shown in Figures 6A and 6B for powder dried at 120°C for 2h. The agglomerate structure was much less densely packed than in the samples precipitated with H₂O₂ alone and consisted of randomly-oriented uniform crystallites 5-8nm in diameter. The powder obtained from this sample after hydrothermal treatment (example C2) is shown in Figures 6C and 6D. The crystallites were uniform and about 5nm in diameter and appeared to

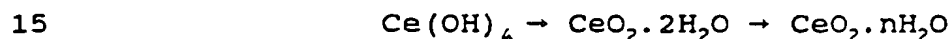
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be loosely agglomerated. After calcination for 1h at 500°C there was very little change in crystallite size.

5 The reference product was powder produced by method A i.e. the precipitation of cerium hydroxide from Ce(III) nitrate by the addition of ammonium hydroxide. The XRD spectra of the precipitate dried at 80°C (example A1) showed that the product consisted of
10 well-crystallised CeO₂ and TG weight loss measurement indicated it to be slightly hydrated, so that a transformation must have occurred on drying the powder e.g.:



This method yielded agglomerates with a wide size distribution and which were hard and non-dispersible after calcination and therefore not suitable for
20 further processing. However, hydrothermal treatment of the wet precipitate (example A2) yielded weakly-agglomerated cubic crystallites that were suitable for further processing. The crystallite size was 15-20nm in size according to TEM images and about 27nm
25 according to XRD peak broadening. The hydrothermal treatment therefore solved the problem of hard agglomerates with this material, but at the expense of considerable crystal growth. In contrast, method C yielded a weakly-agglomerated powder which was not
30 subject to crystal growth during hydrothermal treatment and which had a crystallite size of about 5nm according to XRD measurement and which appeared somewhat smaller in TEM images, although the image magnification was too low for an accurate measurement.



A key feature of the method C was to mix together hydrogen peroxide and cerium (III) nitrate solution as a temperature low enough to prevent immediate reaction e.g. about 5°C. Maintaining the solution at a constant low temperature ensured that subsequent precipitation occurred homogeneously and that a stable sol formed.

The composition of the dried sol particles precipitated with H_2O_2 alone (method B) as deduced from TG was $\text{Ce}(\text{OH})_4/\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ (measured weight loss = 16.8%, theoretical weight loss = 17.3%). Precipitation of a hydroxide in an acidic solution seems unlikely, but it could form during the drying procedure due to the limited stability of lanthanide peroxides. The crystallite size of about 3nm is also an indication that the precipitation mechanism differed from that with ammonium hydroxide which yielded crystallites about 5 times larger. The role of the peroxo ligand during precipitation may have been to reduce the crystallite growth rate by changing the surface properties or morphology of the particles.

Addition of ammonium hydroxide to the sol (method C) resulted in further precipitation of cations from solution to yield an orange precipitate for which a composition of $\text{Ce}(\text{OH})_3\text{OOH}$ was deduced from TG (measured weight loss = 23%, theoretical weight loss = 23.2%). This was the composition deduced for the dried product but, given the uncertainty about the stability of the lanthanide peroxides, it may be more appropriate to describe the precipitate that formed in solution by the general formula $\text{Ce}(\text{OH})_{4-x}\text{OOH}_x$ with $x \geq 1$ for the precipitate formed at 5°C. The $x=1$ composition appeared to be stable enough to withstand drying at 80°C but did not withstand 4h at 100°C. The use of



ammonium hydroxide in the second stage of method C not only completed the precipitation process of method B but also disrupted the dense agglomerates formed by H_2O_2 precipitation as can be seen by comparing Fig 5 and Fig 6. Loosely-agglomerated powder should be less subject to crystallite growth on calcination in proportion to the reduced number of contact points between crystallites. Crystallite growth was insignificant during hydrothermal treatment of samples precipitated with hydrogen peroxide and ammonium hydroxide, and the crystallite size remained under 5nm. In samples precipitated with ammonium hydroxide alone, crystallite size almost doubled to over 25nm under the same conditions. It is difficult to attribute the suppression of crystallite growth during hydrothermal treatment to the continued presence of the peroxo group, which is believed to be unstable at the temperatures used i.e. 180°C. The addition of ammonium hydroxide in method C therefore appears to be an important factor in the prevention of hard agglomerates which might otherwise transform to single crystals on heating as shown in Fig 5G. Crystallites smaller than 5nm were reported previously only in the case of precipitation of $CeOSO_4 \cdot H_2O$ from Ce(IV) sulphate solution. In contrast to the nitrate group, the sulphate group is not easily decomposed on calcination, and sulphate is therefore generally not acceptable in a cerium oxide precursor.

The method of inducing homogeneous precipitation by the oxidation of the cation to a higher valence state with an increased hydrolysability, in this case Ce(III)/Ce(IV), is also applicable to other materials e.g. Fe(II)/Fe(III). An advantage of using of hydrogen peroxide as an oxidising, complexing and precipitating



ligand is that it does not contaminate the end product with additional anion species.

5 The weakly-agglomerated state of the cerium oxide powder, the uniform crystallite size of under 5nm, and the absence of deleterious anion impurities are characteristics which make the powder suitable for a variety of ceramic forming processes and applications.

10 Powders precipitated by the new two-stage method are significantly more weakly agglomerated as well as having a smaller crystallite size i.e. less than 5nm.

15

Table 1:

Crystallite size of cerium oxide powders calculated from XRD peak broadening (Scherrer equation)

20

Sample preparation parameters			Crystallite size (nm) after thermal treatment		
Example	Temp	Autoclaved	12h at 80 - 85°C	1h at 300°C	1h at 500°C
A1	RT	no	15.4	15	27
A2	RT	yes	26.8	27	26
B3	100° C	no	3.2	4.4	-
C1	5°C	no	3.4	5.2	13
C2	5°C	yes	4.2	4.5	10

25



Claims

1. A process for inducing homogeneous precipitation of a metal oxide, wherein said metal is capable of existing in at least two cationic oxidation states, which process comprises the steps of,
5 (i) providing an aqueous solution of a metal in a lower cationic oxidation state and,
10 (ii) adding an oxidant capable of oxidising said metal to a higher cationic oxidation state under conditions such that the mixing of said aqueous solution and said oxidant is substantially complete before precipitation of an oxide of said metal in its higher
15 oxidation state occurs.
2. A process as claimed in claim 1 wherein the metal oxide which precipitates out of solution is a product of hydrolysis of the
20 metal in its higher cationic oxidation state.
3. A process as claimed in claim 1 or claim 2 wherein the oxidant is added as an aqueous
25 solution.
4. A process as claimed in any one of the preceding claims wherein the metal is selected from Ce or Fe.
30
5. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state comprises nitrate as a
35 counter-ion.



- 5 6. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration in the range of from 0.01 to 1.0 mol/l.
- 10 7. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state is of a concentration of approximately 0.1 mol/l
- 15 8. A process as claimed in any one of the preceding claims wherein the oxidant comprises hydrogen peroxide.
- 20 9. A process as claimed in claim 8 wherein the metal salt or oxide has the general formula $M(OH)_{x-y}OOH_y$ wherein x is equal to the oxidation state of the metal cation M and $y \geq 1$.
- 25 10. A process as claimed in claim 8 or claim 9 wherein the metal in its lower oxidation state is Ce^{3+} , the metal in its higher oxidation state is Ce^{4+} and the metal oxide which precipitates has the general formula $Ce(OH)_{4-y}OOH_y$ wherein $y \geq 1$.
- 30 11. A process as claimed in any one of the preceding claims wherein the rate of oxidation is reduced by cooling the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant prior to
- 35 mixing.



12. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant are cooled to a temperature in the range of from -10 to 10°C prior to mixing.
13. A process as claimed in any one of the preceding claims wherein the aqueous solution of said metal in a lower cationic oxidation state and/or the oxidant are cooled to a temperature in the range of from 0 to 5°C prior to mixing.
14. A process as claimed in any one of the preceding claims comprising the additional step of adding hydroxide ions to the reaction mixture so as to substantially complete the precipitation process.
15. A process as claimed in claim 14 wherein said hydroxide ions are provided by the addition of ammonium hydroxide.
16. A process as claimed in any one of the preceding claims comprising the further step of isolating the precipitate.
17. A process as claimed in claim 16 comprising the further step of washing and drying the isolated precipitate.
18. A process for the preparation of a weakly agglomerated nanocrystalline powder of a metal oxide which process comprises the



steps of,

- i) inducing homogeneous precipitation of said metal oxide by a process according to claim 14 or claim 15.
- ii) isolating the precipitate.

5

19. A process as claimed in claim 18 which further comprises the step of subjecting the precipitate to hydrothermal treatment.

10

20. A process as claimed in claim 18 or claim 19 comprising the further step of washing and drying the precipitate.

15

21. A process as claimed in any one of claims 18 to 20 wherein said hydrothermal treatment is at a temperature of from 100 to 300°C.

20

22. A process as claimed in any one of claims 18 to 21 claim wherein said hydrothermal treatment is at a temperature of approximately 180°C.

25

23. A metal oxide obtained by a process as claimed in any one of claims 1 to 17.

30

24. A weakly agglomerated nanocrystalline powder of a metal oxide produced according to a process as claimed in any one of claims 18 to 22.

35

25. A metal oxide as claimed in claim 23 or a weakly agglomerated nanocrystalline powder of a metal oxide as claimed in claim 24 having a mean particle size in the range of



from 2 to 10nm and with a geometric standard deviation in the particle size less than or equal to 1.2.

- 5 26. A metal oxide as claimed in claim 23 or
 claim 25 or a weakly agglomerated
 nanocrystalline powder of a metal oxide as
 claimed in claim 24 or claim 25 having a
10 mean particle size in the range of from 2 to
 5 nm with a geometric standard deviation in
 the particle size less than or equal to 1.1.
27. A metal oxide as claimed in any one of
 claims 23, 25 or 26 or a weakly agglomerated
15 nanocrystalline powder of a metal oxide as
 claimed in any one of claims 24, 25 or 26
 which comprises cerium oxide.
28. A glass, a polishing medium for glass, a
20 thin surface film, a phosphor, an oxygen
 storage material or a catalyst material
 which has been manufactured by a process
 which uses a weakly agglomerated
 nanocrystalline powder of a metal oxide as
25 claimed in any one of claims 24, 25, 26 or
 27.



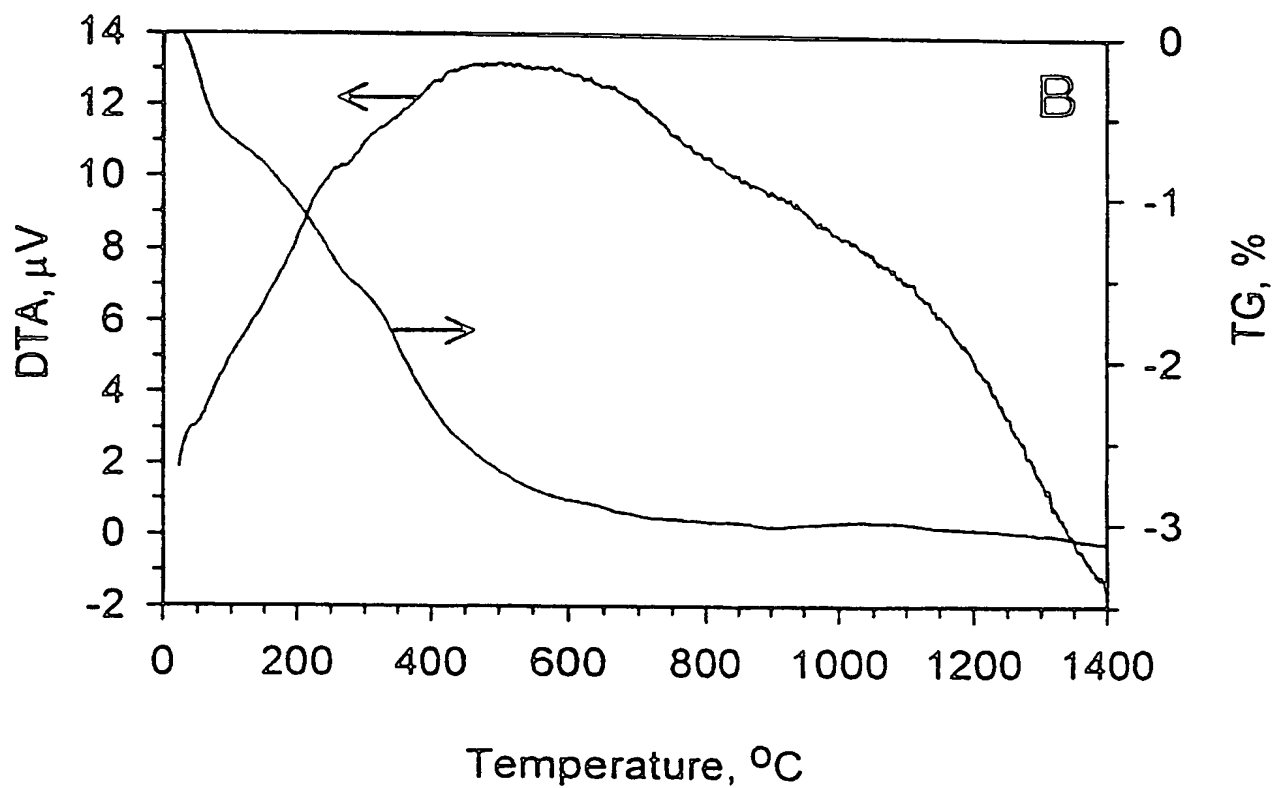
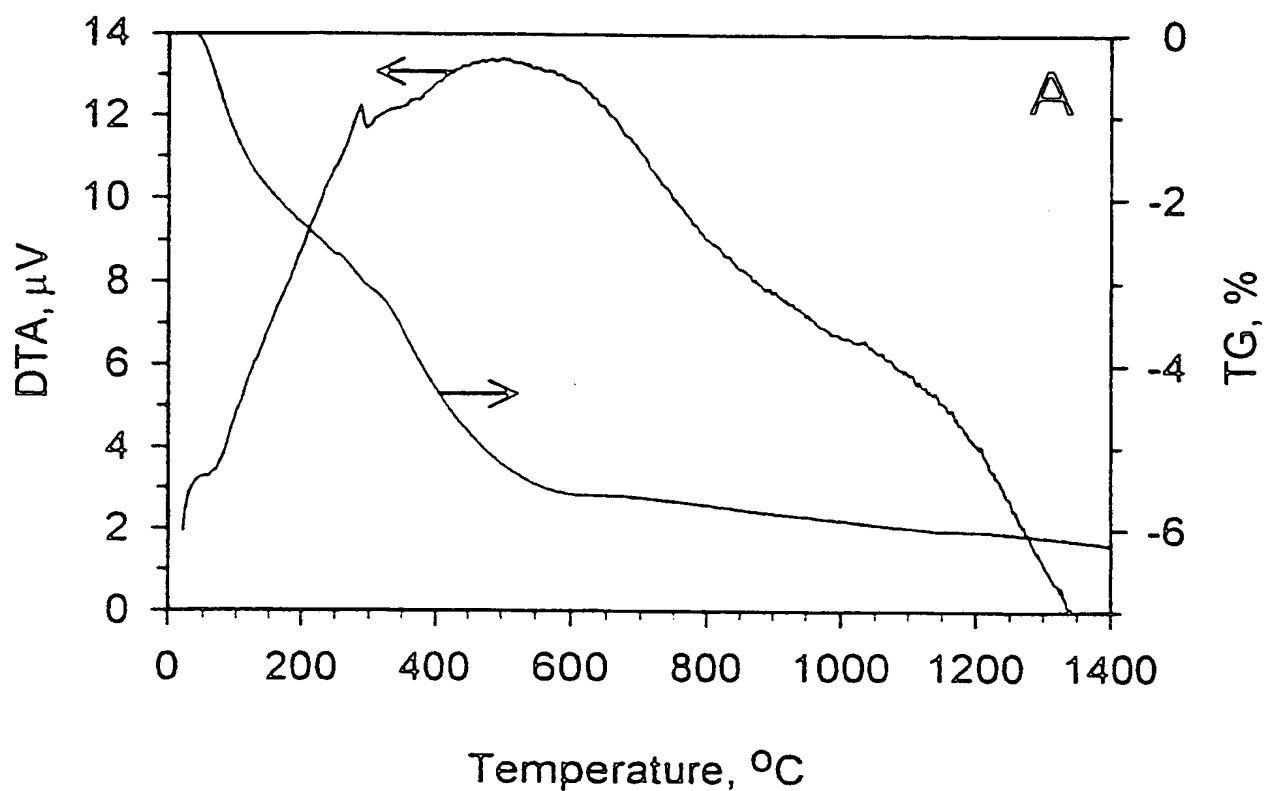


FIG. 1



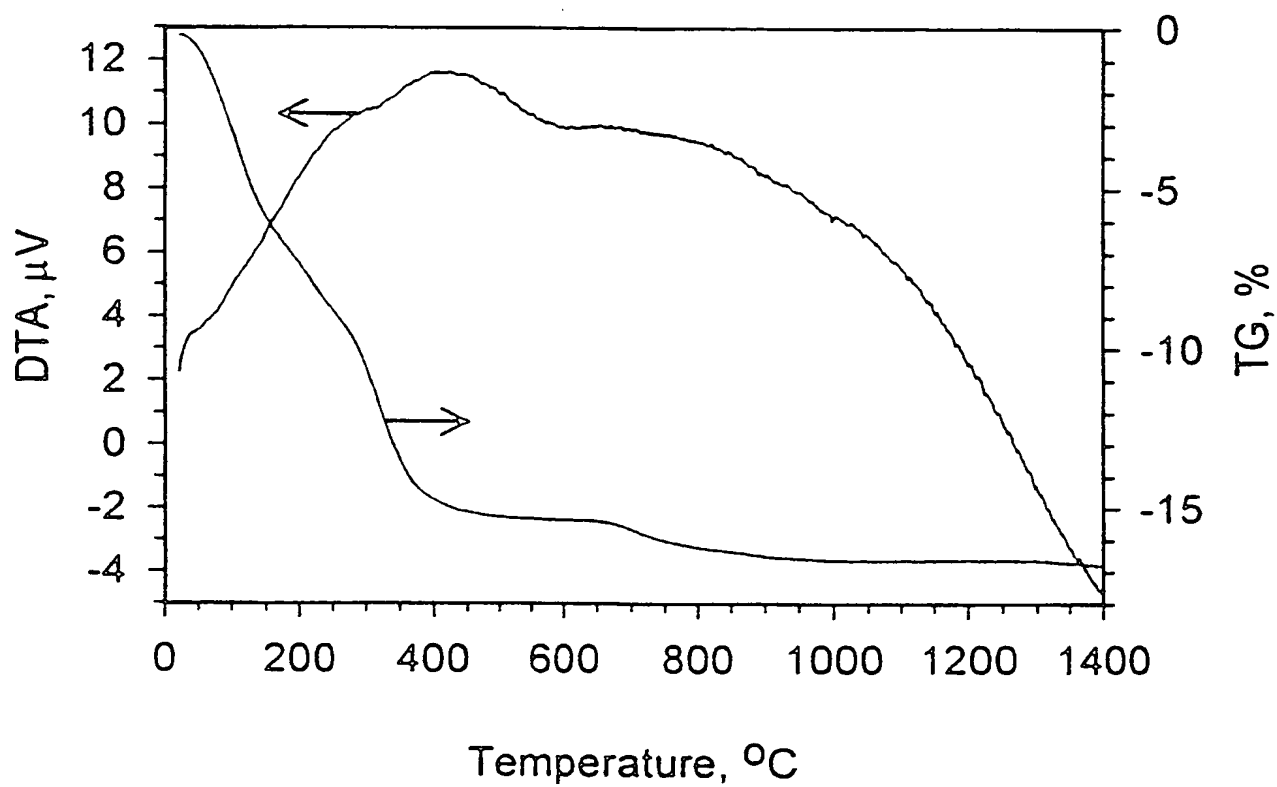


FIG. 2



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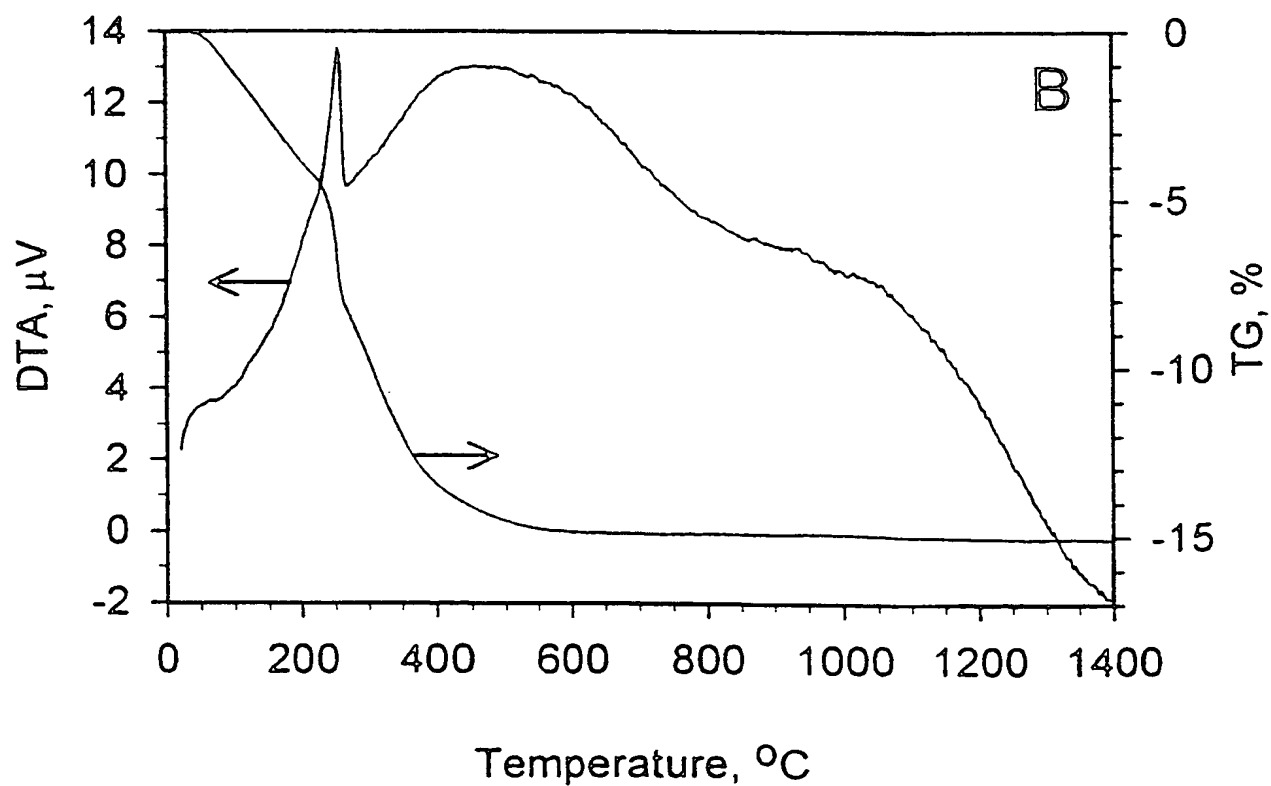
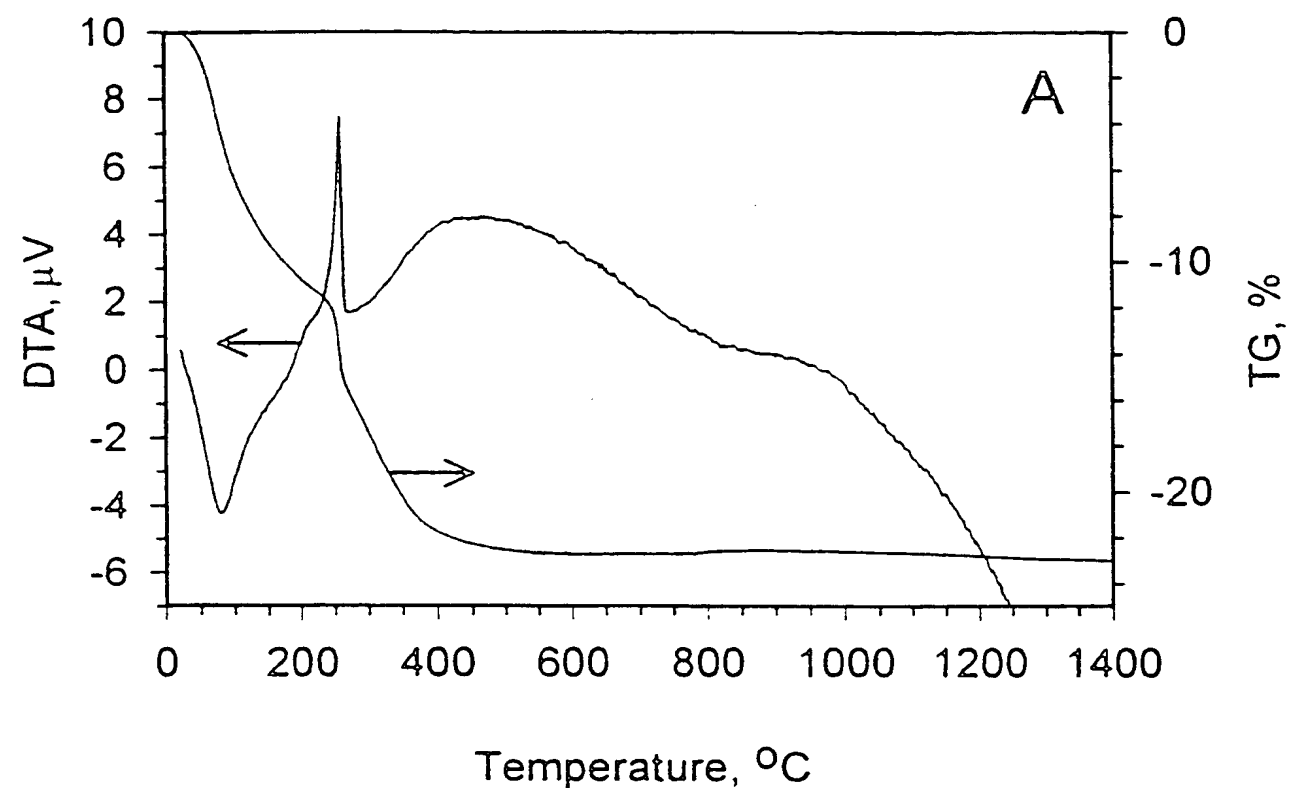


FIG. 3

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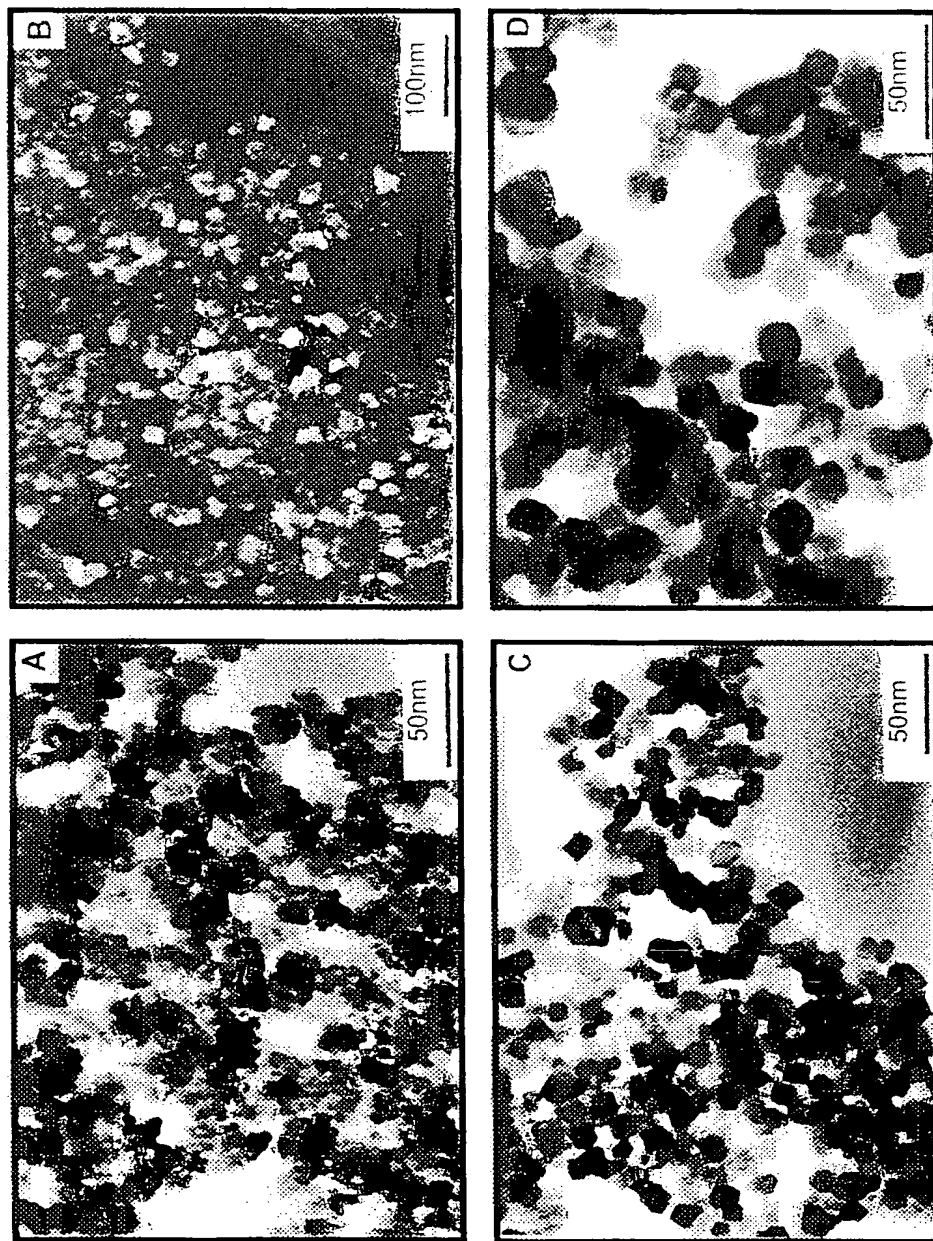


FIG. 4



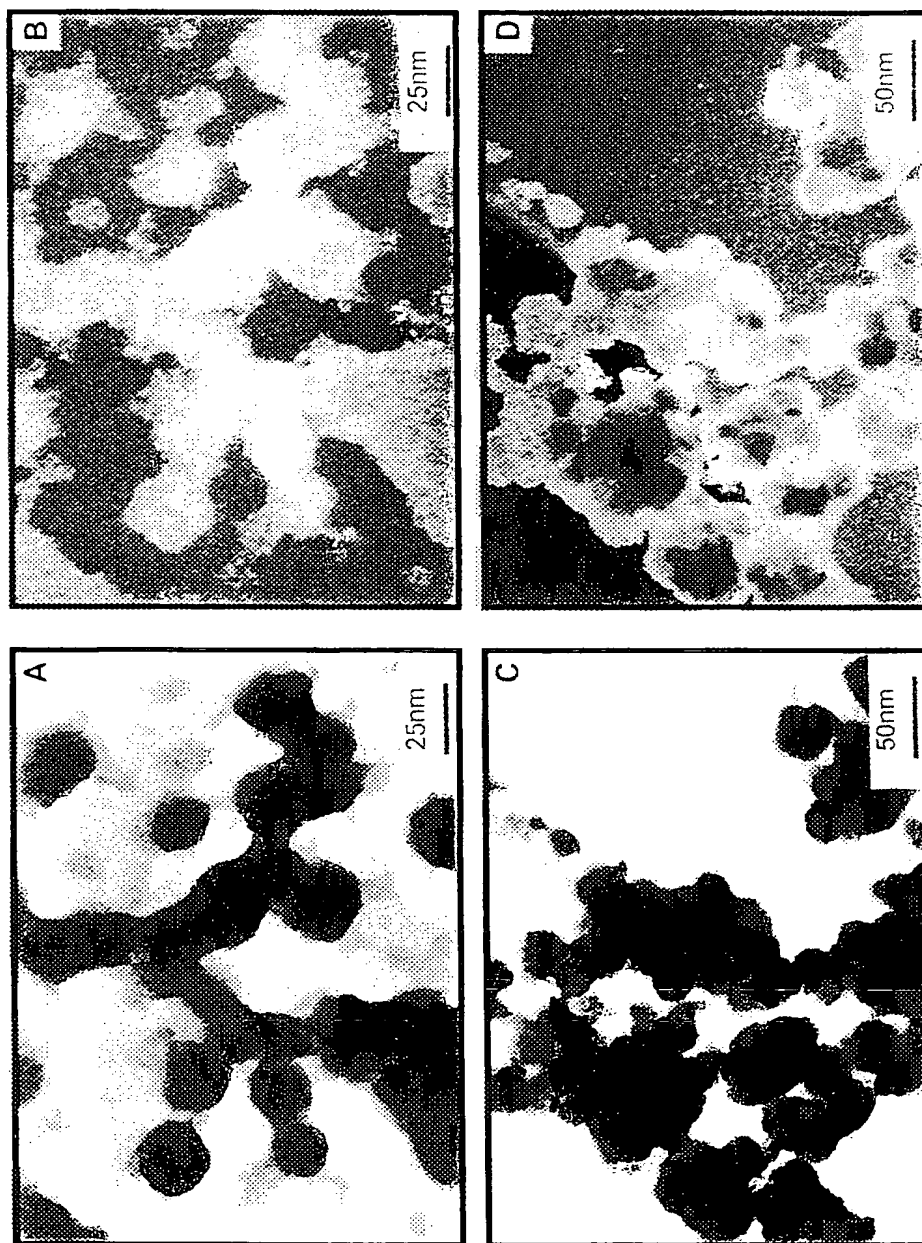


FIG. 5

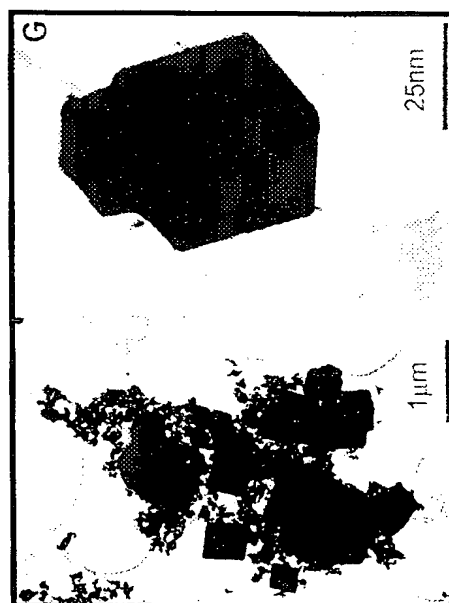
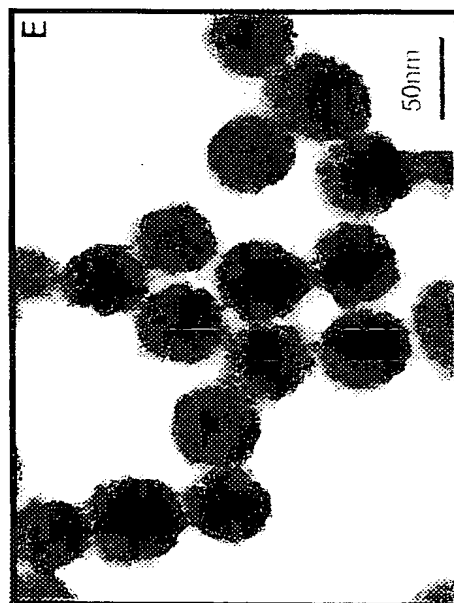
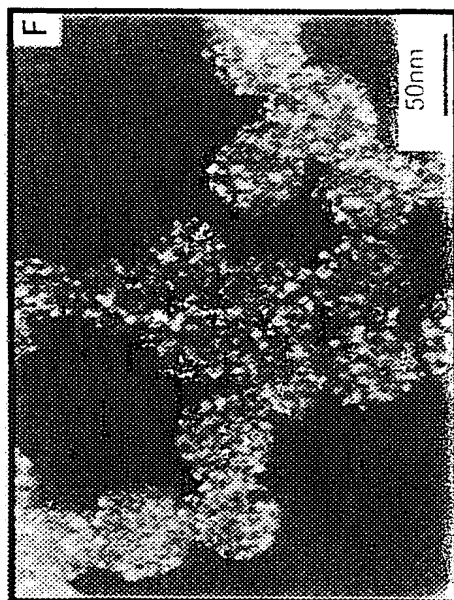


FIG. 5_{CONT'D}

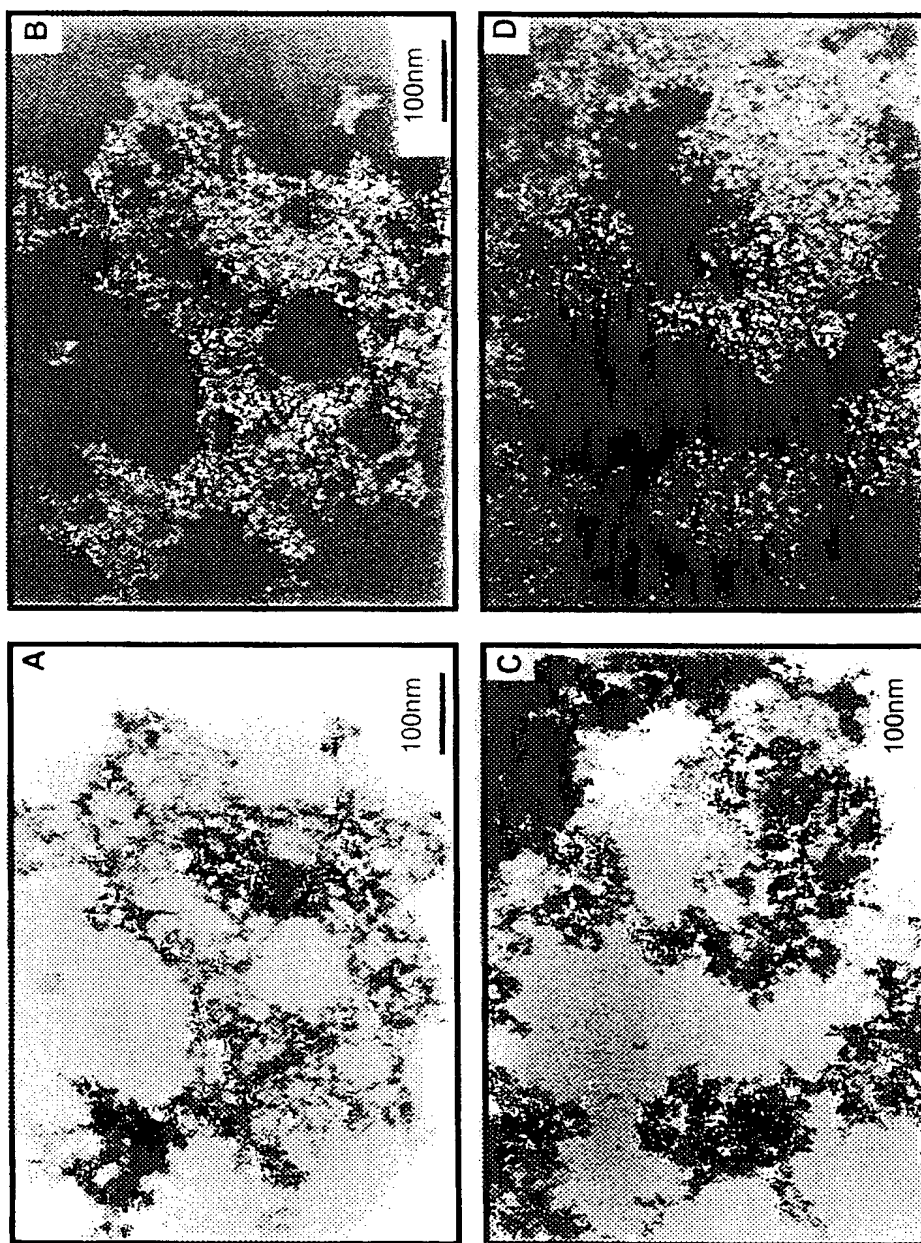


FIG. 6

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/GB 00/00513

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B13/32 C01F17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 03252 A (RODEL INC) 2 February 1995 (1995-02-02) claim 1	1
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 112 (C-0815), 18 March 1991 (1991-03-18) & JP 03 005324 A (KAWASAKI STEEL CORP), 11 January 1991 (1991-01-11) abstract	1
A	US 5 064 791 A (OHTSUKA KUNIO ET AL) 12 November 1991 (1991-11-12) column 4, line 38 - line 57	1
A	EP 0 712 175 A (STARCK H C GMBH CO KG) 15 May 1996 (1996-05-15) page 2, line 19 - line 36	1
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

25 May 2000

Date of mailing of the international search report

05/06/2000

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INTERNATIONAL RCH REPORT

Int  Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 011, no. 202 (C-432), 30 June 1987 (1987-06-30) & JP 62 027310 A (TOKUYAMA SODA CO LTD), 5 February 1987 (1987-02-05) abstract</p> <p style="text-align: center;">---</p>	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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EP 0 518 900 B1

(12)

EUROPEAN PATENT SPECIFICATION

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30.07.1997 Bulletin 1997/31

(51) Int Cl.⁶ **G01L 3/10, G01L 1/16**

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PCT/GB91/00328

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WO 91/13832 (19.09.1991 Gazette 1992/22)

(54) **METHOD AND APPARATUS FOR DYNAMIC TORQUE MEASUREMENT**

VORRICHTUNG UND VERFAHREN ZUR DYNAMISCHEN DREHMOMENTMESSUNG

PROCEDE ET APPAREIL DE MESURE DYNAMIQUE DE COUPLE

(84) Designated Contracting States:
AT BE DE DK FR GB IT LU NL SE

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(43) Date of publication of application:
23.12.1992 Bulletin 1992/52

(56) References cited:
DE-A- 2 950 891 **FR-A- 2 553 884**
US-A- 4 096 740

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- Patent Abstracts of Japan, vol. 8, no. 163 (P-290)(1600), 27 July 1984; & JP-A-5960332 (TOSHIBA K.K.) 6 April 1984
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- Radio, Fernshen Elektronik, vol. 34, no. 8, August 1985, (Ost-Berlin, DE), R. Thomä et al.: "Sensoren auf der Grundlage akustischer Oberflächen-wellen", pages 480-483
- Pages 54 to 58 of the booklet 'Sensortechnik für Kraft und Drehmoment' by E.Baumann, Berlin (DD) 1983

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EP 0 518 900 B1

Description

BACKGROUND

The present invention is particularly concerned with the measurement of dynamic torque arising when power is transmitted by way of a rotating shaft.

TECHNICAL FIELD

For the measurement of static and dynamic strain conventional resistive strain gauges are widely used. They are characterised by resistive elements incorporated into bridge circuit so that changes in resistive elements due to stress in components to which at least some of the elements are secured are quantified by way of the bridge circuit.

A resistive strain gauge can be used for measurement of torque transmitted by a shaft to which the gauge are securely attached. Slip rings on the shaft are used to feed signal inputs to and to recover signal outputs from the gauge. Changes in the geometry of the gauge arising from twisting of the shaft during torque transmission are monitored by way of the slip rings. However the use of slip rings has a number of disadvantages. Brush drag on the slip rings produces errors which are significant for measurement of signals representing lower torque values and drag can vary with the friction conditions and as wear occurs. Inertia effects limit the acceleration to which the shaft bearing the slip rings can be subjected. The rings and brushes generate electrical noise.

The measurement of torques can extend from on the one hand the very small torques arising from viscosity associated with the use of small scale laboratory mixers to, on the other hand, the very large torques occurring in transmission shafts of aero and marine propulsion units. It has been found that in general slip ring systems are not readily applied to the measurement of torque of less than about 2 Newton metre. Typically the diameter of the gauge section of a shaft becomes so small that insufficient area is available to provide for the mounting of strain gauge of suitable size and the size of the electrical noise generated results in a signal to noise ratio which prejudices effective use. At the other extreme on very large shafts the use of slip rings and the associated equipment can lead to access and housing problems.

As an alternative to resistive strain gauges optical torque transducers have become available for the purposes of shaft torque measurement. In an optical transducer radially extending segmented gratings are mounted on the shaft. Output from an array of light sources passes through the gratings to fall on a bank of photocells. The signal output from the photocells varies directly with the torque applied to the shaft. Accuracy of measurement is unaffected by the shaft speed or the torque range. The intensity of the light sources can be moni-

tored to ensure that photocell output does not vary due to light source variation.

Currently these optical/electronic gauges are widely used for torques extending in ranges from 0 to 10 milli Newton metres to 0 to 5000 Newton metres and for rotational speed between 0.5 to 30000 rpm. While the technical advantages of the optical electronic systems are substantial they are costly. In particular the segmented gratings are expensive to manufacture. In addition a periodic need to replace lights in the array imposes a design constraint inasmuch as the gauge needs to be accessible for maintenance and calibration.

BACKGROUND ART

In what follows reference is made to a 'surface acoustic wave resonator'. Such a resonator is made up of a microstructure deposited on a piezoelectric substrate. The microstructure is formed by at least one pair of interleaved comb-like ('interdigitated') electrodes deposited as a thin metal conducting layer on the substrate. Figure 1 shows a basic model of a surface acoustic wave device 10 having input electrode 11 interleaved with output electrode 12. The electrodes are a deposit of aluminium (other good conductors can be used) having a thickness of the order of 1000 Angstroms. The electrodes 11, 12 are deposited on upper surface 14 of a piezoelectric substrate 13. Many piezoelectric materials are suitable for a substrate from flexible plastic polymers to hard materials such as ceramic and quartz. Various piezo electric crystal forms can be used such as lithium niobate, lithium tantalate, bismuth germanium oxide and gallium oxide. Hereafter such a surface acoustic wave device will be referred to as an 'SAW resonator'.

In an SAW resonator the application of an electric signal to one electrode in the pair causes it to act as a transducer converting the electrical input signal into an outgoing acoustic wave on the substrate. The other electrode in the pair reverses the process providing an electrical output signal with the arrival of an acoustic wave on the substrate.

An SAW resonator acts as a 'high Q' device that is to say one in which the selectivity of the circuit is high and narrows the bandwidth passed by the circuit. SAW resonators are among a number of surface acoustic wave devices which are widely used in signal processing applications such as delay lines, frequency filters, bandpass filters, oscillators, duplexers and convolvers. SAW devices are the subject of current research and development. A number of publications are available including 'Surface Acoustic Wave Devices and Their Signal Processing Applications' by Colin Campbell (1989 Edition) published by Academic Press, Incorporated of San Diego, California USA.

JP-A-59-60332 shows a device for the measurement of output torque of a shaft by providing a surface acoustic wave resonator on a flexible beam whose ends

are attached to the shaft by way of rings spaced apart along the shaft. When a torque is applied to the shaft the rings rotate relative to each other to an extent proportional to the torque and the beam bridging the rings deforms so that surface acoustic wave generators located on the beam deform. As a result the output of the generators varies with one being in compression and the other in tension so that one frequency output increases and the other decreases. The resonant frequencies are amplified and transmitted to a receiver by an antenna. While this device facilitates calibration and signal processing for the measurement of output torque it involves the mounting of the rings on the shaft and the attachment of the each end of the beam to a ring (both skilled operations) and for the systems to be subsequently calibrated before being put into use. The addition of the beam necessarily increase the envelope swept out by the rotating shaft. The device is only applicable to a shaft whose speed of rotation will not cause the beam to be displaced outwardly or will not give rise to out of balance oscillations.

French Patent Application FR-A-2553884 shows the use of SAW resonators to measure torque in a cylindrical bar. The bar has a first end face anchored to fixed location and a second end face able to twist about an axis of the bar. The bar in the region of the second end face is equipped with a pair of stems extending perpendicular to the axis and provided with weights at their outer ends remote from the bar. The curved surface of the bar is equipped with at least one pair of SAW resonators laid on a helical path. Each resonator is separately connected to an amplifier. When the bar is not subject to twisting the amplifier provides as output a signal frequency f_0 . When the bar is subject to twisting a different frequency is generated depending on the helical path and the twisting force applied arising from the weights at the outer end of the stems at the outer end of the bar. The bar does not serve to transmit dynamic torque by rotation about the axis but merely twists over its length. Consequently coupling of a resonator on the bar to an amplifier is by direct wiring. In addition in each case each SAW resonator has a separate input and output connection to the or an amplifier.

DISCLOSURE OF THE INVENTION

According to a first aspect of the present invention there is provided a method of measuring dynamic torque wherein at least one pair of surface acoustic wave transducers are mounted on a substrate disposed on a body subject to torque such that the substrate is, and so the transducers are, caused to distort in response to the applied torque providing for the torque to be measured by measuring the distortion of the transducers or a function thereof, the distortion serving to alter the frequency control of the pair of transducers with a consequent change in output frequency related to the applied torque further comprising the steps of:

1 rotating the body about longitudinal axis of the body while the body is transmitting torque to be measured;

2 mounting the generators of the pair on the body as a complementary pair relative to each other and to the body so that for a first direction of rotation of the shaft about the axis one transducer is under compression and the other under tension

3 providing a signal input for each transducer and a common signal output for both transducers of the pair, which inputs and output are located at discrete locations on or near the outside of the body for rotation therewith;

4 causing a driving signal to be applied to each signal input by way of a signal transmitter coupled to the signal input by inductive, capacitive or radio wave means of low power;

5 detecting at the signal output at least an output resonant frequency of one or both transducers when driven by the driving signal by way of a signal receiver coupled to the signal output by way of inductive, capacitive or radio wave means of low power; and

6 processing the output resonant frequency signal from the pair of transducers to derive information as to the strain generated in the transducers arising from stress in the body due to dynamic torque transmitted by the body.

According to a first preferred version of the first aspect the step of detecting an output resonant frequency from the one transducer provides a first signal frequency and an output resonant frequency from the other transducer provides a second signal frequency either or both of the first or second signals being processed prior to a mixing process.

In the case of this first preferred version preferably the output of the mixing process is a signal and there is provided a further ambient temperature reference signal so as to provide for the generation of a signal proportional to the temperature of the shaft material on which the transducers are mounted. Further as a development of this preferable version a second mixing process can be provided wherein an output frequency of the mixing process is fed to the second mixing process together with a reference signal such that the second mixing process provides as output a sum signal or a difference signal which is a temperature related frequency for scale corrections.

According to a second aspect of the present invention there is provided apparatus for measuring dynamic torque transmitted by a body having an axis of rotation wherein a pair of surface acoustic wave transducers are located relative to a body as a complementary pair with the transducers located directly on the body;

a first signal input and a signal transmitter coupled to the signal input by inductive, capacitive or radio

wave means of low power;

a second signal input and a signal receiver coupled to the signal input by way of inductive, capacitive or radio wave means of low power; and

a signal output common to the outputs of both transducers and a signal receiver coupled to signal output by way of inductive, capacitive or radio wave means of low power;

each transducer being located at discrete locations on or near the outside of the shaft for rotation therewith; each transducer comprising a piezoelectric substrate having mounted on one side a pair of interdigitated electrodes one electrode of the pair being connected to the signal input;

a first generator for applying an input signal at a predetermined frequency to the signal input;

a second generator for applying an input signal at a predetermined frequency to the signal input; and a mixer for receiving a signal from the first generator and signal from the second generator whereby changes in signal output from strain applied to the substrate can be derived.

According to a first preferred version of the second aspect of the present invention the mixer is adapted to receive a discrete output resonant frequency from the one transducer and a discrete output resonant frequency from the other transducer and to mix both signals or derivatives thereof to produce a composite signal derived from both the signals or from derivatives thereof. preferably the signal mixer is adapted to provide as signal outputs a sum and difference signal derived from the output of the transducer pair the difference signals being a function of measured torque and the sum signal being a function of the ambient temperature in the region of the transducers. The difference signal and the sum signal or derivatives thereof can be fed to a common processor.

In a given fundamental unstrained state of the substrate and the electrodes mounted upon it a signal input fed to the input electrode results in the transmission of a surface acoustic wave to the output electrode with a characteristic resonant frequency output signal from the output electrode. In the event the substrate is subject to strain then the consequent change in the relative geometry of the electrode array results in the resonant output frequency being subject to change which can be detected and related to the amplitude of the strain or a function of it. This is capable of wide application since given a source of stress which can be transmitted into strain in the substrate the source can be analysed by way of signal changes resulting from geometry changes in the SAW transducer.

The operational frequencies of an SAW resonator can be selected anywhere in a wide frequency range extending from a few megahertz up to few gigahertz. The higher the frequency used the smaller the envelope required for the transducer which can be of particular

benefit in strain related applications where available space is limited. The resonant frequency used depends on a number of factors including the geometry of the electrodes and properties of the substrate material. The velocity of the surface wave varies with the temperature of the substrate material. The very small sizes in which an SAW resonator can be made facilitates its use as a strain measuring device in a wide range of applications.

Coupling between the electrodes can be by 'surface acoustic' (also known as Rayleigh) waves. For such waves the substrate needs to have a smooth propagation surface for two reasons in particular. Firstly surface defects could cause breaks in individual parts of the electrodes affecting frequency response. Secondly the surface wave energy is concentrated within a layer one or two wavelengths thick.

Another acoustic propagation mode which can be used to couple the electrodes are 'surface skimming bulk' waves. These extend more deeply into the substrate than the surface acoustic waves and consequently the surface skimming bulk waves have higher losses than arises with the surface acoustic mode. However the bulk waves are less sensitive to defects in the substrate surface.

The choice of operating mode will depend on the strain measurement to be undertaken.

An SAW resonator can be used in a system where signal inputs to the transducer input and signal outputs from the transducer are transmitted by non-contact coupling (such as by inductive, capacitive or radio wave means) to an external control system. The provision of a noncontact coupling where the electrodes have no direct electrical connection provides a number of advantages particularly when there is a need for intrinsic safety or where physical connection would affect the resonance to be measured. Such non-contact systems are particularly convenient for rotating mechanisms. An SAW transducer can be used in place of a resistive strain gauge. In any event an SAW strain transducer is capable of a degree of accuracy substantially greater than that of a conventional resistive strain gauge.

The electrode array in an SAW resonator can take a number of forms though all provide for an accurate and specific relationship between operating frequency and electrode geometry.

A single port SAW resonator requires only two connections for operation. Conveniently such a transducer is used with an amplifier having a negative input resistance characteristic so that a state of oscillation can be maintained by an impedance change in the SAW resonator.

A two-port resonator has lower losses than a corresponding single port type, can be made to operate in a multi-mode fashion and has advantages with regard to phase shift making it applicable to high precision applications.

Amongst other advantages arising from the invention is the provision of temperature evaluation in con-



nection with torque measurement. This will be discussed later in connection with torque measurement will be discussed later in relation to processing output signals from SAW transducers. Typically an SAW transducer can be used in connection with a bi-metallic strip where the coefficient of expansion of one metal making up the strip differs from that of the other. In the event of a temperature change the strain on one side of the strip will be compressive and on the other side tensile. Consequently by mounting an SAW resonator on each strip the frequency difference between their outputs will be the representative of the ambient temperature due to material strain. Alternatively the sum of the frequencies will be a measure of temperature due to material expansion. For such a device operating power levels lower than 1 mW can be used which, in combination with a non-contact coupling, would meet intrinsic safety requirements.

BRIEF DESCRIPTION OF DRAWINGS

A number of exemplary embodiments of the present invention will now be described with reference to the accompanying drawings of which:

Figure 1 is a diagrammatic view of a transducer;
Figure 2 is a circuit diagram of a transducer similar to those described in connection with Figures 1 combined with an amplifier;

Figure 3 is a diagrammatic view of a twinned pair of transducers of the type shown in Figure 1;

Figure 4 is a circuit diagram of a twinned pair of transducers similar to those described in connection with Figure 3 combined with an amplifier;

Figure 5 is a circuit diagram incorporating the components described in connection with Figure 4 coupled to additional components to provide for compensation and correction;

Figure 6 is a circuit diagram showing the coupling of transducers described in earlier figures to an output device;

Figure 7 is an application of the system shown in Figure 6; and

Figure 8 is a further development of the circuitry described in connection with Figure 7.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

The exemplary embodiments described in relation to Figures 3 to 8 show the use of one or more SAW resonators to measure dynamic torque.

In order to measure torque the substrate of each resonator is securely attached to the shaft or other strain transmitting member under test. This can either be directly or by way of an interface between the substrate and the test piece such as might be needed, for example, where the resonator is encapsulated for protection

of the resonator components against a hostile environment. Torque (radial strain) is measured by a change in the output frequency of the resonator arising from a change in shape of the substrate element and so in the relative positions of the electrodes deposited upon the substrate. The radial strain is induced by the stress in the shaft under test and is proportional to the applied torque.

The temperature coefficient of an SAW resonator can be very low. Its frequency of oscillation can be up to about 1 Gig Hertz (10^9 Hz). A typical frequency would be 500 MHz and therefore a change of 0.1% would produce a frequency change of 500 KHz (5×10^5).

Figure 1

This shows a shaft S to which has been secured the substrate of an SAW resonator transducer T. The centreline C of the transducer T is located at 45 degrees to longitudinal axis A of the shaft S. If the applied torque is applied clockwise from the right hand end of the shaft S (as shown by arrow K) the transducer T is placed in tension. If the torque direction was reversed the transducer T is placed in compression.

Figure 2

Transducer T of the type shown in Figure 1 is connected with an amplifier A. The circuit will oscillate at a given frequency when the amplifier provides for the correct phase shift for, and with enough gain to overcome losses occurring in, the resonator and coupling.

Figure 3

Two SAW resonator transducers T1 and T2 are mounted as shown on the shaft S with their centre lines X1 and X2 at right angles to one another. Torque applied to the shaft in clockwise direction shown by arrow K will induce compressive stress in transducer T1 and tensile stress in transducer T2. Any temperature changes would apply equally to both elements. An alternative paired arrangement is with the two transducers mounted on opposite sides of the shaft again with their centrelines at right angles to one another (and at 45 degrees to the axis of the shaft).

Figure 4

A pair of transducers T1 and T2 are mounted on a shaft as shown in Figure 3. Transducers T1 and T2 are coupled with, respectively, amplifiers A1 and A2 which provide output signal frequencies, respectively, F1 and F2. The output signal are fed to a mixer M having an output F. The output frequency F will be $F1 + F2$ and $F1 - F2$. Ignoring the $F1 + F2$ component a typical frequency difference of 1 MHz would be generated for a change of 0.1% due to applied torque. Output from the transducers

is only proportional to torque and with no torque being transmitted $F_1 - F_2$ will be close to zero. Changes in the geometry of the transducers T1 and T2 due to temperature or end load effects will apply equally to both so that the net result will be zero.

The tensile strength of virtually any material is temperature dependent. Consequently a knowledge of the ambient temperature will enable correction or compensation to be made. Thus the output F , ($F_1 + F_2$), of mixer M will, if compared with a reference, produce a signal frequency proportional to temperature of the material to which the substrate of each transducer is attached.

Figure 5

This circuit incorporates one similar to that of Figure 4. Components referred to in connection with Figure 4 are given the same reference in Figure 5. In addition Figure 5 shows a further mixer M2 and a reference signal generator R to enable temperature corrections to be applied. Output frequency $F_1 + F_2 (= A)$ of mixer M is fed to mixer M2 together with a signal B, typically 1 GHz, from generator R. As a result mixer M2 provides as output sum $A + B$ or $A - B$. The difference signal is at a frequency related to temperature and can be used to correct scale factors in precision applications.

As SAW devices operate in ultra-high frequency regions finite impedance matching is required to obtain the most efficient coupling. In the present context this amounts to an impedance of the order of 50 ohms. The device described in connection with Figures 3, 4 and 5 are directionally insensitive with a typical loss of 18 dB.

Figure 6

This shows how energy is coupled to each of the SAW resonator transducers T1 and T2 by way of a coil and a probe. Coils C1-C3 are each fitted to the shaft S for rotation with it and are coupled to transducers T1 and T2. The coils can be designed to give more than one peak amplitude per shaft revolution as would be appropriate for low speed applications such as ship propeller shafts. Static probes P1-P3 are mounted adjacent the shaft. Coil P1 and associated probe P1 serve as a common output for the transducers T1, T2, coils C2, C3 and associated probes P2, P3 serve as inputs, respectively to transducer T1 and transducer T2. The necessary matching impedance is 50 ohms for the coils C1 to C3 and to probes P1 to P3. Amplifiers A1 and A2 must provide adequate gain for their associated circuitry to oscillate taking into account the space loss between each coil and probe combination. Each amplifier is provided with automatic gain control ('AGC') to accommodate reasonable system losses such as can arise from changes in distance between coil and probe. Power dividers R1, R2 serve to regulate frequencies fed to mixer M. The SAW resonators do not have to be harmonically related. Any frequency difference out of mixer M can be

reduced by making use of a further mixer.

Figure 7

This shows a practical embodiment of a control arrangement based on Figure 6. Since the transducers are positioned on the shaft as shown in Figure 6 they are consequently not shown in Figure 7. Coils C1 to C3 serve to transmit signals to probes P1 to P3 as described in connection with Figure 6. Diodes D1 and D2 change impedance with applied voltage to provide an AGC effect. On the output voltage from an amplifier increasing it is rectified and used to provide a control current to pin diodes D1, D2 so reducing diode resistance and so causing levelling of the amplifier output which in turn produces a constant frequency output from the resonator.

Further information can be provided from the output of the transducer arrangement. Thus shaft rotational speed can be represented by amplitude modulation of pin diode control current if coil C1 is made eccentric with respect to the shaft so generating an output related to each shaft revolution. For slowly rotating shafts (such as a ship's propeller shaft) a coil or coils can be used to generate a number of outputs per shaft revolution (an output for a given angular displacement of the shaft).

Figure 8

Circuitry shown and described in connection with Figure 6 and 7 are here combined together with additional features. Where a component shown in Figure 8 is similar in form and function to one shown in Figure 6 and/or 7 it is given the same reference.

Shaft S is equipped with transducers T1 and T2 which are coupled by way of coils C1 and C2 and probes P1 and P2 to the remainder of the control circuitry. In this case the output frequency of T1 is 250 MHz and that of transducer T2 500 MHz. Amplifier A1 feeds its output of 250 MHz to frequency doubler D from which an output signal of 500 MHz is fed to Mixer M. Amplifier A2 feeds its output frequency of 500 MHz to mixer M directly. Output of mixer M, representing $(500 + 500)$ MHz and $(500-500)$ MHz is split. The difference signal (representing a torque signal) is fed directly to a microprocessor MP by way of line 10. The sum signal (providing a temperature signal) is fed to a second mixer M2 by way of line 11. The mixer M2 also receives by way of line 12 a reference input signal of 1 GHz. The output of the mixer M2 representing a temperature signal which is fed by way of line 13 to the microprocessor MP to enable the microprocessor to provide for a temperature compensated output. As a consequence the microprocessor MP provides an output to display W showing the speed of rotation, the transmitted torque, and the power transmitted by the shaft S under test with due temperature compensation.

The transducer pairs shown in Figures 3, 6 and 8

are mounted at 90 degrees to one another and 45 degrees to the shaft. Other mounting angles can be used. Typically to enable shaft load measurements to be checked the two transducers while being mounted at right angles to one another could be mounted with one transducer parallel to the axis of the shaft. In this way the transducer parallel to the shaft axis will be sensitive to the effect of axial loads on the shaft.

The embodiments make use of probe/coil coupling between the shaft mounted transducers and the control circuitry. However for use in static measurements the transducers could be coupled by wires to the control circuitry.

The exemplary embodiments, and particularly that described in connection with Figure 8, provide for strain measuring systems offering substantial advantages over existing devices.

The transducer of the present invention in addition to being small in size and capable of very accurate outputs provide for low manufacturing cost and to large scale production. A strain gauge transducer based on the SAW device makes use either of existing components or, as in the case of the SAW itself, of an electrode deposition process which is capable of being manufactured more cheaply and with greater inherent accuracy than existing transducer components (such as resistance gauges or apertured disks). In addition the mounting of the components is more readily achieved than with existing strain gauge or optical torque measuring devices.

In one form the transducer would be encapsulated to protect the electrodes and working circuitry. The transducer is attached to the item whose stressing is of concern typically by welding or adhesive to ensure that the substrate material is as tightly secured as possible so that the maximum transmission of strain occurs from the test piece to the substrate.

An SAW resonator can be made small in size and mass. As a consequence inertia effects are minimal in contrast to currently available systems which in the main involve the mounting of inertially significant components. Because of the low size and mass the system can accommodate a wide variety of operating conditions. The proposed SAW resonator system provides for high accuracy and sensitivity achieved by the use of what amounts to frequency modulating techniques making use of solid state components having high reliability and of low power consumption. The associated control and processing equipment utilise available signal processing methods and components which are readily interfaced with existing digital processes and equipment. Typically in the case of torque measurement there are virtually no limitations imposed by the shaft mounted part of the system on the speed at which the shaft under test can be rotated or at which it can be accelerated or decelerated. The system will also provide valid data from start-up from zero shaft speed on start up and for very low shaft speeds.

The proposed SAW resonator system of the present invention is inherently safe since only signal strength power is used. This contrasts with, for example, currently available torque measurement by way of an optical system requiring the use of sufficient power for a plurality of lamps.

Claims

1. A method of measuring dynamic torque wherein at least one pair of surface acoustic wave transducers (T1, T2) are mounted on a substrate disposed on a body (S) subject to torque such that the substrate is, and so the transducers are, caused to distort in response to the applied torque providing for the torque to be measured by measuring the distortion of the transducers or a function thereof, the distortion serving to alter the frequency control of the pair of transducers with a consequent change in output frequency related to the applied torque further comprising the steps of:

1 rotating the body (S) about longitudinal axis (A) of the body while the body (S) is transmitting torque to be measured;

2 mounting the generators (T1, T2) of the pair on the body (S) as a complementary pair relative to each other and to the body (S) so that for a first direction of rotation (K) of the shaft (S) about the axis (A) one transducer is under compression and the other vector tension

3 providing a signal input (C2, C3) for each transducer (T1, T2) and a common signal output (C1) for both transducers (T1, T2) of the pair, which inputs (C2, C3) and output (C1) are located at discrete locations on or near the outside of the body (S) for rotation therewith;

4 causing a driving signal to be applied to each signal input (C2, C3) by way of a signal transmitter (P2, P3) coupled to the signal input (C2, C3) by inductive, capacitive or radio wave means of low power;

5 detecting at the signal output (C1) at least an output resonant frequency of one or both transducers (T1, T2) when driven by the driving signal by way of a signal receiver (P1) coupled to the signal output (C1) by way of inductive, capacitive or radio wave means of low power; and

6 processing the output resonant frequency signal (C1) from the pair of transducers (T1, T2) to derive information as to the strain generated in the transducers (T1, T2) arising from stress in the body (S) due to dynamic torque transmitted by the body (S).

2. A method of measuring dynamic torque as claimed

in Claim 1 wherein the step of detecting an output resonant frequency from the one transducer (T1) provides a first signal frequency (f1) and an output resonant frequency from the other transducer (T2) provides a second signal frequency (f2) either or both of the first or second signals being processed (R1, R2) prior to a mixing process (M).

3. A method of measuring dynamic torque as claimed in Claim 2 wherein the output of the mixing process (M) is a signal and there is provided a further ambient temperature reference signal so as to provide for the generation of a signal proportional to the temperature of the shaft material on which the transducers are mounted.

4. A method of measuring dynamic torque as claimed in Claim 3 wherein a second mixing process (M2) such that an output frequency of the mixing process (M) is fed to the second mixing process (M2) together with a reference signal (B) such that the second mixing process (M2) provides as output a sum signal (A + B) or a difference signal (A - B) which is a temperature related frequency for scale corrections.

5. Apparatus for measuring dynamic torque transmitted by a body (S) having an axis of rotation (A) wherein a pair of surface acoustic wave transducers (T1, T2) are located relative to a body as a complementary pair with

the transducers (T1, T2) located directly on the body (S); a first signal input (C2) and a signal transmitter (P2) coupled to the signal input (C2) by inductive, capacitive or radio wave means of low power;

a second signal input (C3) and a signal receiver (P2) coupled to the signal input (C3) by way of inductive, capacitive or radio wave means of low power; and

a signal output (C1) common to the outputs of both transducers (T1, T2) and a signal receiver (P1) coupled to signal output (C1) by way of inductive, capacitive or radio wave means of low power;

each transducer (T1, T2) being located at discrete locations on or near the outside of the shaft (S) for rotation therewith; each transducer (T1, T2) comprising a piezoelectric substrate (13) having mounted on one side a pair of interdigitated electrodes (11, 12); one electrode (11) of the pair being connected to the signal input (C2, C3);

a first generator (A1, R1) for applying an input signal at a predetermined frequency to the signal input (C2);

a second generator (A2, R2) for applying an in-

put signal at a predetermined frequency to the signal input (C3); and

a mixer (M) for receiving a signal from the first generator (A1, R1) and signal from the second generator (A2, R2) whereby changes in signal output (C1) from strain applied to the substrate (13) can be derived.

6. Apparatus for measuring dynamic torque as claimed in Claim 5 wherein the mixer (M) is adapted to receive a discrete output resonant frequency (f1) from the one transducer (T1) and a discrete output resonant frequency (f2) from the other transducer (T2) and to mix both signals or derivatives thereof to produce a composite signal derived from both the signals (f1, f2) or from derivatives thereof.

7. Apparatus for measuring dynamic torque as claimed in Claim 6 wherein the signal mixer (M) adapted to provide as signal outputs a sum and difference signal derived from the output (C1) of the transducer pair (T1, T2), the difference signals being a function of measured torque and the sum signal being a function of the ambient temperature in the region of the transducers.

8. Apparatus for measuring dynamic torque as claimed in Claim 7 wherein the difference signal and the sum signal or derivatives thereof, are fed to a common processor (MP).

Patentansprüche

1. Verfahren zum Messen des dynamischen Drehmoments, bei dem mindestens ein Paar akustische Oberflächenwellen-Wandler (T1, T2) an einem Substrat angebracht sind, das sich an einem einem Drehmoment ausgesetzten Körper (S) befindet, so daß das Substrat und mithin die Wandler ansprechend auf ein aufgebrachtes Drehmoment verzerrt werden, so daß das Drehmoment dadurch meßbar ist, daß die Verzerrung der Wandler oder eine Funktion der Verzerrung gemessen wird, wobei die Verzerrung dazu dient, die Frequenzsteuerung des Wandlerpaares zu ändern, womit eine Änderung der Ausgangsfrequenz in bezug auf das aufgebrachte Drehmoment einhergeht, weiterhin umfassend die Schritte:

1) Drehen des Körpers (S) um eine Längsachse (A) des Körpers, während der Körper (S) zu messendes Drehmoment überträgt;

2) Anbringen der paarweisen Wandler (T1, T2) an dem Körper (S) als Komplementär-Paar zueinander und zu dem Körper (S) derart, daß bei einer ersten Drehrichtung (K) der Welle (S) um



die Achse ein Wandler unter Druckspannung und der andere unter Zugspannung steht:

- 3) Bereitstellen eines Signaleingangs (C2, C3) für jeden Wandler (T1, T2) und eines gemeinsamen Signalausgangs (C1) für beide Wandler (T1, T2) der Paares, wobei die Eingänge (C2, C3) und der Ausgang (C1) sich an diskreten Stellen an oder in der Nähe der Außenseite des Körpers (S) befinden, um sich damit zu drehen: 5
- 4) Veranlassen, daß an jeden Signaleingang (C2, C3) über einen Signalsender (P2, P3), der mit dem Signaleingang (C2, C3) über eine induktive, kapazitive oder Funkwellen-Einrichtung geringer Leistung gekoppelt ist, ein Treibersignal gelegt wird: 10
- 5) Nachweisen an dem Signalausgang (C1) mindestens eine Ausgangsresonanzfrequenz eines Wandlers oder beider Wandler (T1, T2) bei deren Ansteuerung durch das Treibersignal, mit Hilfe eines Signalempfängers (P1), der an den Signalausgang (C1) mit Hilfe einer induktiven, kapazitiven oder Funkwellen-Einrichtung geringer Leistung gekoppelt ist: und 15
- 6) Verarbeiten des Ausgangs-Resonanzfrequenzsignals (C1) von dem Paar von Wandlern (T1, T2), um Information bezüglich der in den Wandlern (T1, T2) erzeugten Verformung, die aus Spannung in dem Körper (S) aufgrund des auf den Körper (S) übertragenen dynamischen Drehmoments resultiert. 20
2. Verfahren zum Messen des dynamischen Drehmoments nach Anspruch 1, bei dem der Schritt des Nachweisens einer Ausgangsresonanzfrequenz von dem einen Wandler (T1) eine erste Signalfrequenz (f1) liefert, und einer Ausgangsresonanzfrequenz von dem anderen Wandler (T2) eine zweite Signalfrequenz (f2) liefert, wobei das erste und/oder das zweite Signal vor einem Mischprozeß (M) verarbeitet (R1, R2) werden. 25
3. Verfahren zum Messen des dynamischen Drehmoments nach Anspruch 2, bei dem die Ausgangsgröße des Mischprozesses (M) ein Signal ist und es ein weiteres, Umgebungstemperatur-Referenzsignal gibt, um ein Signal zu bilden, welches proportional ist zu der Temperatur des Wellenmaterials, an dem die Wandler angebracht sind. 30
4. Verfahren zum Messen des dynamischen Drehmoments nach Anspruch 3, bei dem ein zweiter Mischprozeß (M2) vorgesehen ist, so daß eine Ausgangsfrequenz des Mischprozesses (M) den zweiten Mischprozeß (M2) gemeinsam mit einem Referenz-

signal (B) zugeführt wird, damit der zweite Mischprozeß (M2) als Ausgangsgröße ein Summensignal ($A + B$) oder ein Differenzsignal ($A - B$) liefert, bei dem es sich um eine auf die Temperatur bezogene Frequenz für Skalierungskorrekturen handelt.

5. Vorrichtung zum Messen eines dynamischen Drehmoments, das auf einen Körper (S) mit einer Drehachse (A) übertragen wird, wobei ein Paar akustische Oberflächenwellen-Wandler (T1, T2) relativ zu einem Körper als Komplementärpaar angeordnet sind, wobei die Wandler (T1, T2) sich direkt an dem Körper (S) befinden:

ein erster Signaleingang (C2) und ein Signalsender (P2), der mit dem Signaleingang (C2) über eine induktive, kapazitive oder Funkwelleneinrichtung geringer Leistung gekoppelt ist, vorgesehen sind;

ein zweiter Signaleingang (C3) und ein mit dem Signaleingang (C3) über eine induktive, kapazitive oder Funkwellen-Einrichtung geringer Leistung gekoppelter Signalempfänger (P2) vorgesehen sind; und

ein Signalausgang (C1) gemeinsam für die Ausgänge beider Wandler (T1, T2) und ein mit dem Signalausgang (C1) über eine induktive, kapazitive oder Funkwellen-Einrichtung geringer Leistung gekoppelter Signalempfänger (P1) vorgesehen sind;

wobei jeder Wandler (T1, T2) sich an diskreten Stellen an oder in der Nähe der Außenseite der Welle (S) befindet, um sich mit ihr zu drehen, jeder Wandler (T1, T2) ein piezoelektrisches Substrat (13) aufweist, bei dem auf einer Seite ein Paar Interdigitalelektroden (11, 12) angebracht ist, von denen eine Elektrode (11) mit dem Signaleingang (C2, C3) verbunden ist;

ein erster Generator (A1, R1) vorgesehen ist, um ein Eingangssignal einer vorbestimmten Frequenz an den Signaleingang (C2) zu legen; ein zweiter Generator (A2, R2) vorgesehen ist, um ein Eingangssignal vorbestimmter Frequenz an den Signaleingang (C3) zu legen; und ein Mischer (M) ein Signal von dem ersten Generator (A1, R1) und ein Signal von dem zweiten Generator (A2, R2) empfängt, wodurch Änderungen im Signalausgang (C1) aus der auf das Substrat (13) einwirkenden Beanspruchung abgeleitet werden können. 35

6. Vorrichtung zum Messen des dynamischen Drehmoments nach Anspruch 5, bei der der Mischer (M) dazu ausgebildet ist, eine diskrete Ausgangsresonanzfrequenz (f1) von dem einen Wandler (T1) und eine diskrete Ausgangsresonanzfrequenz (f2) von dem anderen Wandler (T2) zu empfangen und beide Signale oder davon abgeleitete Signale zu mi-

schen, um ein zusammengesetztes Signal zu erzeugen, welches von den beiden Signalen (f1, f2) oder davon abgeleiteten Signalen abgeleitet ist.

7. Vorrichtung zum Messen des dynamischen Drehmoments nach Anspruch 6, bei der der Signalmischer (M) dazu ausgebildet ist, als Signalausgänge ein Summen- und ein Differenzsignal zu liefern, die von dem Ausgang (C1) des Wandlerpaares (T1, T2) abgeleitet sind, wobei die Differenzsignale eine Funktion des gemessenen Drehmoments und das Summensignal eine Funktion der Umgebungstemperatur im Bereich der Wandler ist.
8. Vorrichtung zum Messen des dynamischen Drehmoments nach Anspruch 7, bei der das Differenzsignal und das Summensignal oder davon abgeleitete Signale einem gemeinsamen Prozessor (MP) zugeführt werden.

Revendications

1. Procédé de mesure d'un couple dynamique, dans lequel au moins deux transducteurs (T1, T2) à ondes acoustiques de surface sont montés sur un substrat disposé sur un corps (S) soumis à un couple afin que le substrat se déforme et en conséquence que les transducteurs se déforment aussi sous l'action du couple appliquée, en donnant le couple à mesurer par mesure de la distorsion des transducteurs ou d'une fonction de cette distorsion, la distorsion étant utilisée pour la modification du réglage en fréquence des deux transducteurs avec un changement correspondant de la fréquence de sortie liée au couple appliqué, comprenant en outre les étapes suivantes :
 - 1) l'entraînement en rotation du corps (S) autour d'un axe longitudinal (A) du corps alors que le corps (S) transmet le couple à mesurer,
 - 2) le montage des générateurs des deux transducteurs (T1, T2) sur le corps (S) sous forme d'une paire complémentaire l'un de l'autre et du corps (S) afin que, pour un premier sens de rotation (K) de l'arbre (S) autour de l'axe (A), un transducteur soit en compression et l'autre en tension vectorielle,
 - 3) la formation d'une entrée de signaux (C2, C3) pour chaque transducteur (T1, T2) et d'une sortie commune de signaux (C1) pour les deux transducteurs (T1, T2) de la paire, les entrées (C2, C3) et la sortie (C1) étant à des emplacements séparés à l'extérieur du corps (S) ou près de l'extérieur du corps (S) afin qu'elles tournent avec lui,
 - 4) l'application d'un signal de pilotage à chaque entrée de signaux (C2, C3) à l'aide d'un émet-

teur de signaux (P2, P3) couplé à l'entrée de signaux (C2, C3) par un dispositif inductif, capacitif ou à hautes fréquences de faible puissance,

5) la détection de la sortie de signaux (C1) à au moins une fréquence de résonance de sortie de l'un au moins des transducteurs (T1, T2) lorsqu'il est piloté par le signal de pilotage par l'intermédiaire d'un récepteur de signaux (P1) couplé à la sortie de signaux (C1) à l'aide d'un dispositif inductif, capacitif ou à hautes fréquences de faible puissance, et

6) le traitement du signal de sortie à une fréquence de résonance (C1) de la paire de transducteurs (T1, T2) pour la dérivation d'informations relatives à la déformation créée dans les transducteurs (T1, T2) et provenant de la contrainte dans le corps (S) due au couple dynamique transmis par le corps (S)

2. Procédé de mesure d'un couple dynamique selon la revendication 1, dans lequel l'étape de détection d'une fréquence de résonance de sortie du premier transducteur (T1) donne une première fréquence de signaux (f1) et d'une fréquence de résonance de sortie de l'autre transducteur (T2) donne une seconde fréquence de signaux (f2), l'un des premiers et seconds signaux ou les deux étant traités (R1, R2) avant une opération de mélange (M).
3. Procédé de mesure d'un couple dynamique selon la revendication 2, dans lequel la sortie de l'opération de mélange (M) donne un signal, et un signal supplémentaire de référence de température est transmis afin qu'il assure la création d'un signal proportionnel à la température pour le matériau de l'arbre sur lequel sont montés les transducteurs.
4. Procédé de mesure d'un couple dynamique selon la revendication 3, dans lequel une seconde opération de mélange (M2) est telle qu'une fréquence de sortie de l'opération de mélange (M) est transmise à la seconde opération de mélange (M2) avec un signal de référence (B) tel que la seconde opération de mélange (M2) donne en sortie un signal somme (A + B) ou un signal différence (A - B) qui est une fréquence liée à la température et assurant des corrections d'échelle.
5. Appareil de mesure d'un couple dynamique transmis par un corps (S) ayant un axe de rotation (A) entre deux transducteurs (T1, T2) à ondes acoustiques de surface positionnés par rapport à un corps sous forme d'une paire complémentaire, les transducteurs (T1, T2) étant placés directement sur le corps (S),

une première entrée de signaux (C2) et un

émetteur de signaux (P2) couplé à l'entrée (C2)
 par un dispositif inductif, capacitif ou à hautes
 fréquences à faible puissance.
 une seconde entrée de signaux (C3) et un ré-
 cepteur de signaux (P2) couplé à l'entrée de si- 5
 gnaux (C3) par un dispositif inductif, capacitif
 ou à hautes fréquences de faible puissance, et
 une sortie de signaux (C1) commune aux sor-
 ties des deux transducteurs (T1, T2) et un ré- 10
 cepteur de signaux (P1) couplé à la sortie de
 signaux (C1) par un dispositif inductif, capacitif
 ou à hautes fréquences de faible puissance,
 chaque transducteur (T1, T2) occupant un em-
 placement séparé sur l'extérieur de l'arbre (S) 15
 ou près de celui-ci afin qu'il tourne avec lui, cha-
 que transducteur (T1, T2) comprenant un subs-
 trat piézoélectrique (13) sur un côté duquel est
 montée une paire d'électrodes imbriquées (11, 20
 12), une électrode (11) de la paire étant con-
 nectée à l'entrée de signaux (C2, C3).
 un premier générateur (A1, R1) destiné à ap-
 pliquer un signal d'entrée à une fréquence pré-
 déterminée à l'entrée de signaux (C2).
 un second générateur (A2, R2) destiné à appli- 25
 quer un signal d'entrée à une fréquence prédé-
 terminée à l'entrée de signaux (C3), et
 un mélangeur (M) destiné à recevoir un signal
 du premier générateur (A1, R1) et un signal du
 second générateur (A2, R2) si bien que les 30
 changements de sortie de signaux (C1) dus à
 la déformation appliquée au substrat (13) peu-
 vent être dérivés.

6. Appareil de mesure d'un couple dynamique selon 35
 la revendication 5, dans lequel le mélangeur (M) est
 destiné à recevoir une fréquence discrète de réso-
 nance de sortie (f1) du transducteur (T1) et une fré-
 quence discrète de résonance de sortie (f2) de
 l'autre transducteur (T2) et à mélanger les deux si- 40
 gnaux ou leurs dérivées pour la production d'un si-
 gnal composite dérivé des signaux (f1, f2) ou de
 leurs dérivées.
7. Appareil de mesure d'un couple dynamique selon 45
 la revendication 6, dans lequel le mélangeur de si-
 gnaux (M) est destiné à donner, comme sortie de
 signaux, un signal somme et un signal différence
 dérivés de la sortie (C1) de la paire de transduc-
 teurs (T1, T2), les signaux de différence étant fonc- 50
 tion du couple mesuré et le signal somme étant
 fonction de la température ambiante dans la région
 des transducteurs.
8. Appareil de mesure d'un couple dynamique selon 55
 la revendication 7, dans lequel le signal de différen-
 ce et le signal somme, ou leurs dérivées, sont trans-
 mis à un processeur commun (MP).

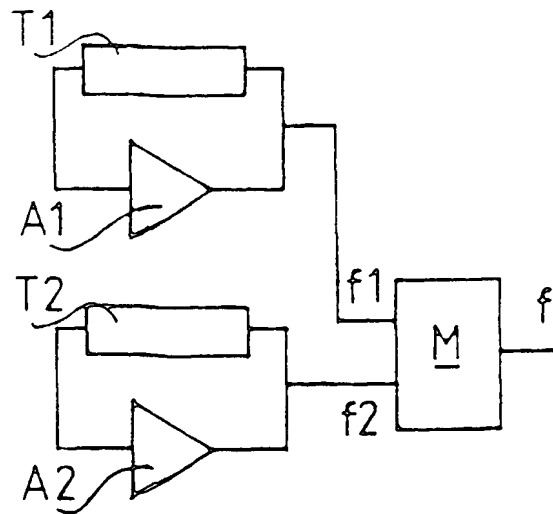
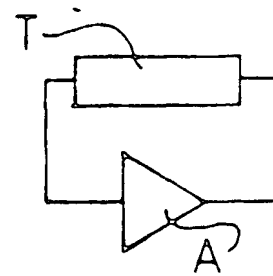
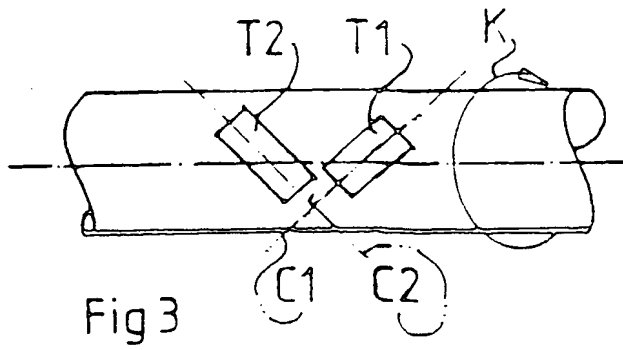
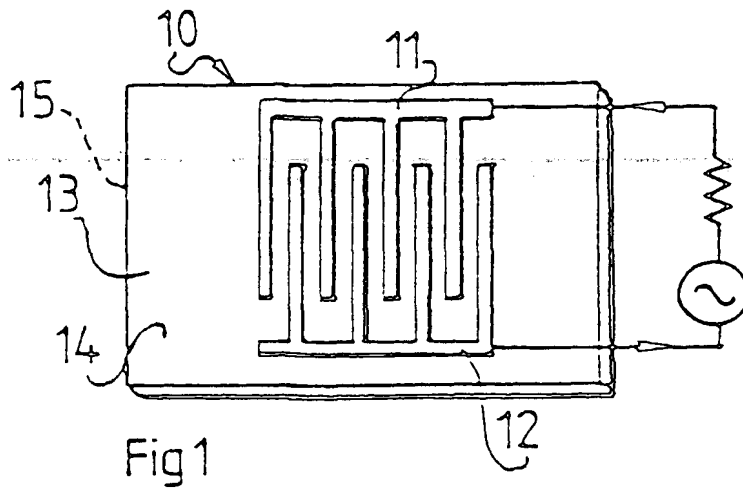


Fig 4

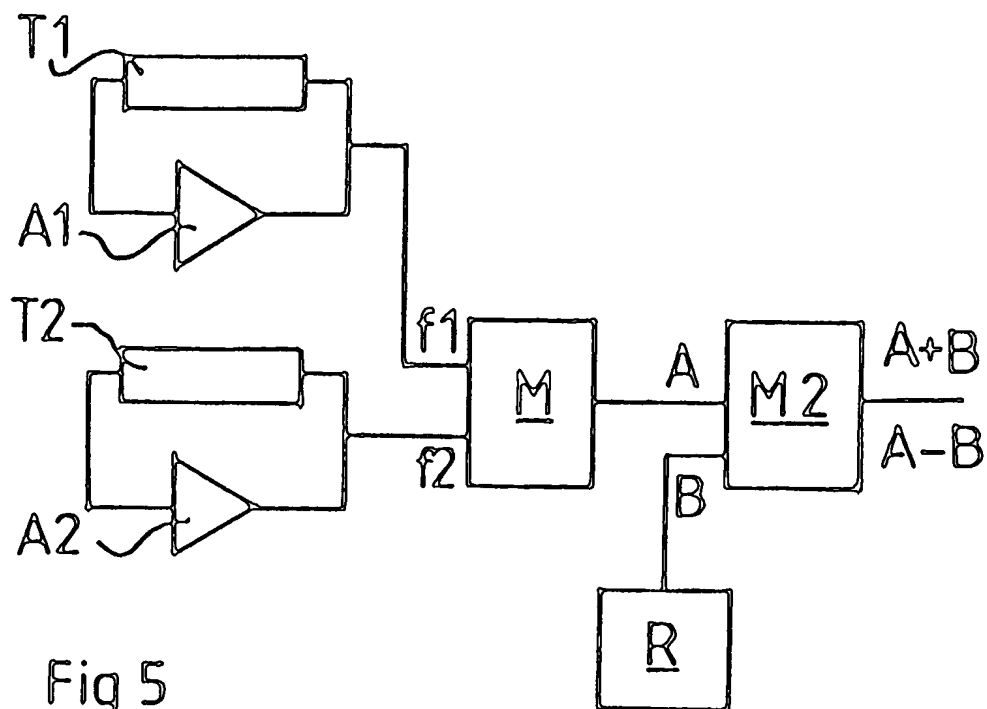


Fig 5

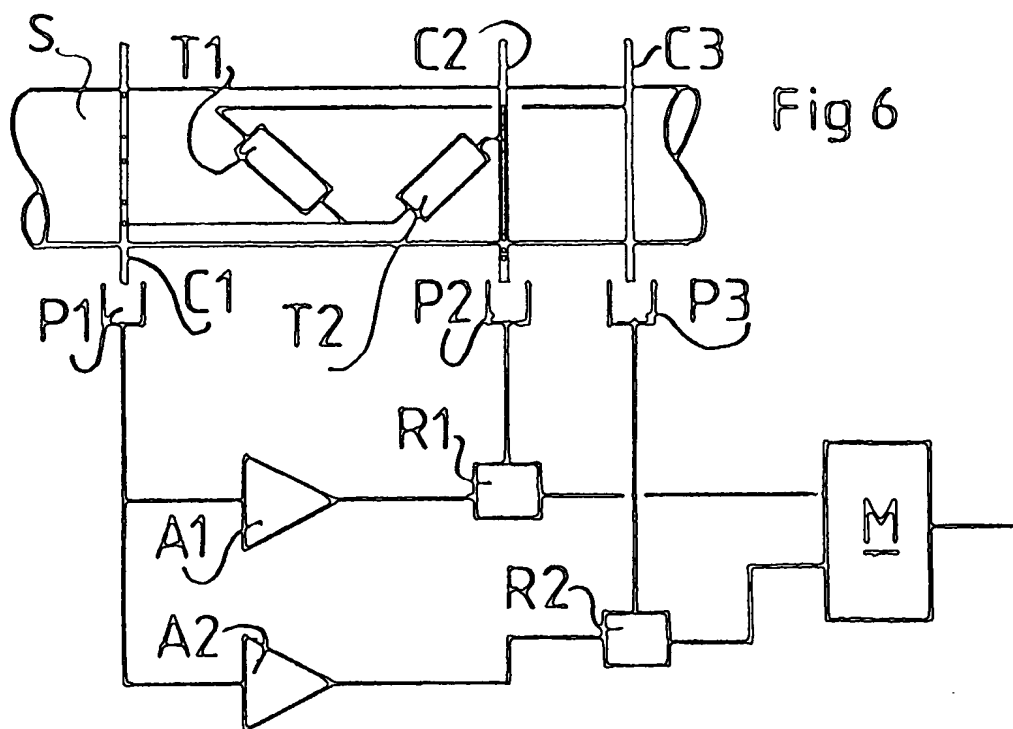


Fig 6

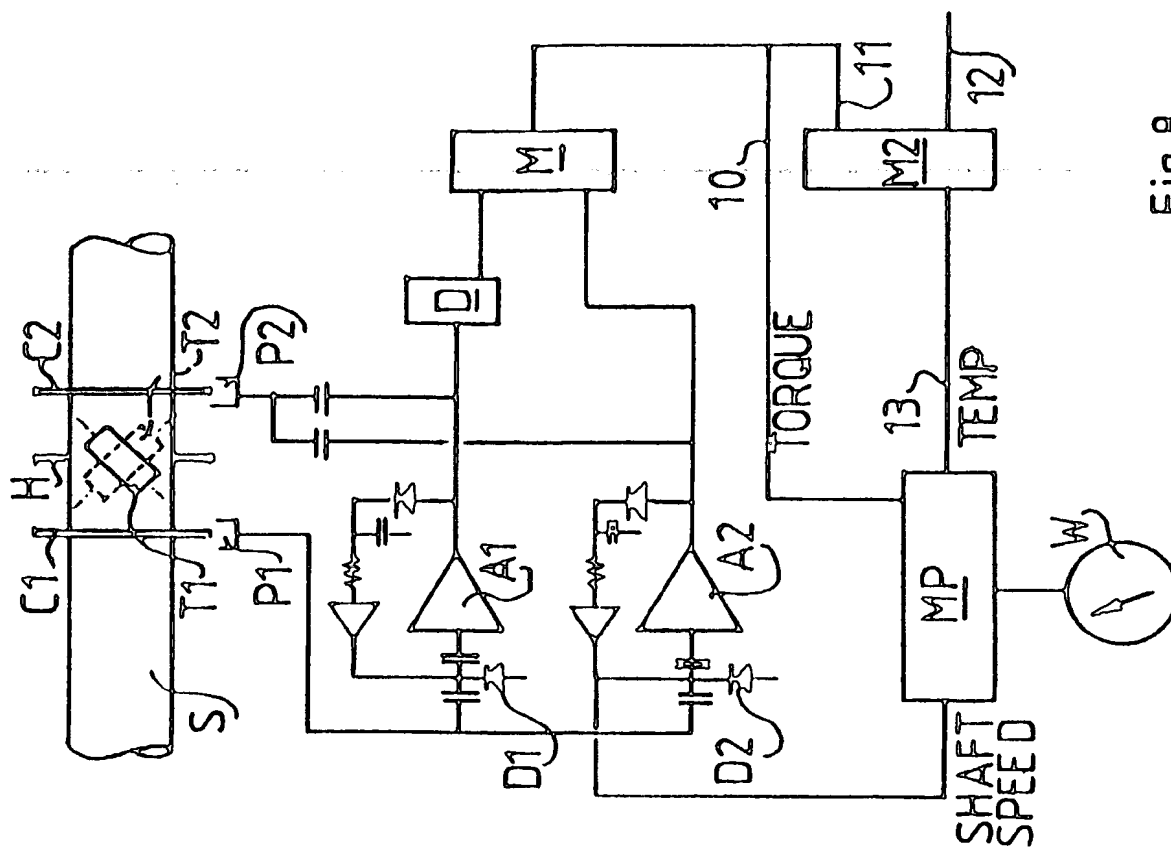


Fig 8

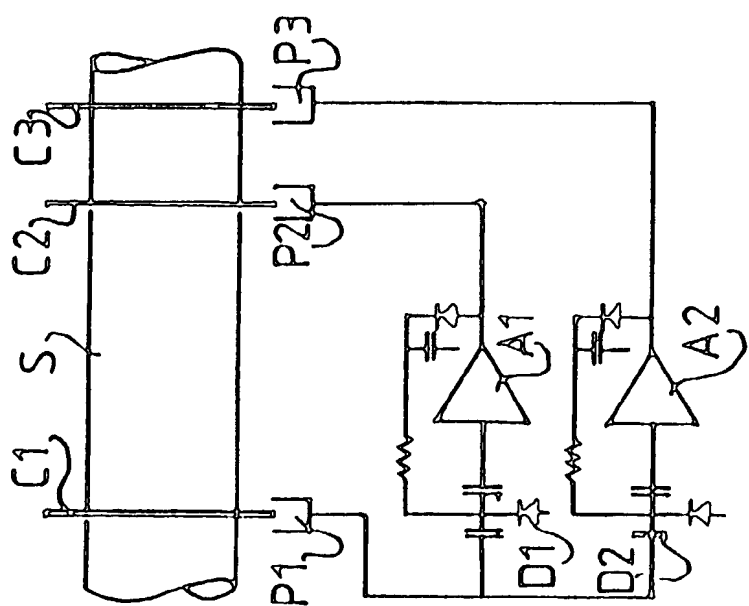


Fig 7

INTERNET COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference PERRY/PD	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/GB 00/ 00298	International filing date (day/month/year) 03/02/2000	(Earliest) Priority Date (day/month/year) 03/02/1999
Applicant PERRY, James, Anthony, Harold		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of Invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 00/ 00298

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

A transducer has a closure for components mounted on the substrate (13) comprising: a lid component (16); and a peripheral component (17) of plastics material secured by one side to the lid component (16) and by the other side to the one side to the substrate (13); the lid component (16) and the peripheral component (17) serve to define a hermetically sealed enclosure (18) for the electrode structure (12). The invention further comprises a workpiece bearing the transducer to enable strain generated in the workpiece to be examined by way of the transducer.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 00/00298

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01L1/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 518 900 B (LONSDALE ANTHONY ; LONSDALE BRYAN (GB)) 30 July 1997 (1997-07-30) cited in the application column 11, line 31 - line 37 ----	1-5,7
Y	US 4 139 859 A (LEWIS TERRENCE E ET AL) 13 February 1979 (1979-02-13) column 3, line 1 - line 13; figures ----	1-5,7
A	US 5 337 026 A (BORCHELT EARL F ET AL) 9 August 1994 (1994-08-09) abstract; figure 3A -----	1

☐ Further documents are listed in the continuation of box C.


Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 May 2000

Date of mailing of the international search report

02/06/2000

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Authorized officer

Nobrega, R.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00298

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0518900 B	23-12-1992	AU 655764 B BR 9106101 A DE 69127074 D DE 69127074 T EP 0518900 A US 5585571 A AT 156262 T AU 7334191 A CA 2077085 A DK 518900 T WO 9113832 A	12-01-1995 24-02-1993 04-09-1997 22-01-1998 23-12-1992 17-12-1996 15-08-1997 10-10-1991 04-09-1991 09-03-1998 19-09-1991
US 4139859 A	13-02-1979	US 3999285 A	28-12-1976
US 5337026 A	09-08-1994	US 5594979 A	21-01-1997

